FORMATION OF INORGANIC SUBMICRON PARTICLES
UNDER SIMULATED PULVERIZED COAL COMBUSTION CONDITIONS

by
Matthew Neville
B.S., University of New Hampshire
(1977)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF
DOCTOR OF SCIENCE

at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
August, 1982

Signature of Author ____________________________

Certified by ____________  Adel F. Sarofim, Thesis Advisor

Accepted by ____________  Glenn C. Williams, Chairman
Departmental Committee on Graduate Theses

Archives
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEC  3 1982
LIBRARIES
FORMATION OF INORGANIC SUBMICRON PARTICLES
UNDER SIMULATED PULVERIZED COAL COMBUSTION CONDITIONS

by

Matthew Neville
Professor Jack P. Ruina  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dear Professor Ruina:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled, "Formation of Inorganic Submicron Particles Under Simulated Pulverized Coal Combustion Conditions", in partial fulfillment of the requirements for the Degree of Doctor in Science in Chemical Engineering at Massachusetts Institute of Technology.

Respectfully submitted,

Matthew Neville
FORMATION OF INORGANIC SUBMICRON PARTICLES
UNDER SIMULATED PULVERIZED COAL COMBUSTION CONDITIONS

by

Matthew Neville

Submitted to the Department of Chemical Engineering in August, 1982 in partial fulfillment of the requirements for the Degree of Doctor of Science from the Massachusetts Institute of Technology

ABSTRACT

The factors governing the physico-chemical characteristics of the inorganic submicron particles produced by the combustion of coal have been examined by burning size-graded Montana lignite particles in a laminar flow drop-tube furnace at 1700 K. The particle combustion temperature achieved vary from 1800 K to 2800 K as the oxygen concentration in which the coal particles burn is increased from 5 percent to 100 percent.

Size fractionation of the ash yields a bimodel size distribution. The average size of the primary particles in the submicron mode varies from less than 50 angstroms to greater than 400 angstroms, depending on the combustion conditions. The submicron particles are produced by vaporization of the mineral matter species during combustion and their subsequent recondensation. The amount of fume produced as metal oxide increases from 0.1 percent at 1800 K to 20 percent at 2800 K. The growth of the submicron particles is well predicted by classical coagulation theory where theory provides a good representation of the observed primary particle size as a function of residence time and degree of ash vaporization. In the early stages of coagulation the particles coalesce, but as the temperature in the vicinity of the particles decreases subsequent to the completion of combustion of the char and as the primary particle diameter increases, the coalescence rate decreases and the agglomerate produced appears as aggregates of spheres.

The chemical composition of the Montana lignite fume is dominated by MgO and CaO at all but the lowest particle combustion temperature (< 1900 K), apparently because the vaporization of these refractory oxides is augmented by their chemical reduction to the more volatile metal vapor in the locally reducing atmosphere within the burning char particle. The inorganic submicron particles are found to consist of a core of MgO, CaO, and FeO with an inner coating of silica and an outer coating of sodium, arsenic, and other trace metals. Furthermore, silicon and the volatile and trace species show an increase in concentration with decreasing particle size in the submicron range (< 400 angstroms).

From a steady state one dimensional model the reoxidation of the vaporized reduced-state species of Mg, Ca, and Fe away from the char surface results in the supersaturation of these refractory oxides in the boundary layer of the burning char particle which is predicted to provide the necessary driving for the formation of a new condensed phase by homogeneous nucleation. Silicon deposition subsequently occurs as a probable consequence of the low rate of oxidation of the SiO vapors released by the
burning coal particle. The volatile and trace species condense on the outer surface as the combustion products are cooled. Most of the ash surface is provided by submicron particles even though they constitute only a small fraction of the total ash. Both the residual and submicron particles are coated with a surface deposit of volatile (Na) and trace (As,Sb) elements. The distribution of the volatile elements between the two size modes of the ash is influenced by the amount of submicron particles produced during combustion and the rate at which the combustion products are cooled. However, in the case of the trace species, where an insufficient driving force for diffusion-controlled condensation exists, the surface deposition of these species is believed to be chemically controlled. Consequently, the distribution of the trace species between the two size modes is influenced by both the relative reactivity and surface area between the two size modes.

Thesis Advisor: Adel F. Sarofim
Professor of Chemical Engineering
ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to his advisor, Professor Adel F. Sarofim, for his continued encouragement, guidance, and enthusiasm throughout the course of this thesis, without which the attaining of this educational goal would not have been possible. The principles in which Professor Sarofim has instilled in the author have made a lasting impression.

Special gratitude is also extended to Richard J. Quann, Anthony J. Modestino, Charles A. Mims, and Brian S. Haynes for their support, advise, and assistance with the experimental and conceptual aspects of this study. The Author is also grateful to John Martin for his assistance with Auger Spectroscopy and ESCA, Professor Vander Sande and Tony Garret-Ried for their assistance with Scanning Transmission Electron Microscope, and Morteza Janghorbani for the Neutron Activation Analysis Service.

This work was supported by Electric Power Research Institute and N.I.E.H.S.

To all members of my family, the author cannot express enough appreciation for their encouragement and support.

Finally, I wish to thank the members of my office and
the members of the combustion group with special gratitude to Myongsook Lee, Lyle Timothy, Harvey Stanger, and Kim Ritrievi for their continued support and encouragement through the course of this thesis work.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>i</td>
</tr>
<tr>
<td>AUTHORIZATION PAGE</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>iv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xv</td>
</tr>
<tr>
<td>CHAPTER ONE. SUMMARY</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Experimental Apparatus</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Results</td>
<td>6</td>
</tr>
<tr>
<td>1.3.1 Dependence of Concentration on Particle Size</td>
<td>6</td>
</tr>
<tr>
<td>1.3.2 Surface Enrichment</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Discussion</td>
<td>15</td>
</tr>
<tr>
<td>1.4.1 Particle Nucleation</td>
<td>15</td>
</tr>
<tr>
<td>1.4.2 Particle Growth</td>
<td>21</td>
</tr>
<tr>
<td>1.4.3 Heterogeneous Condensation</td>
<td>25</td>
</tr>
<tr>
<td>1.5 Conclusions</td>
<td>37</td>
</tr>
<tr>
<td>CHAPTER TWO. BACKGROUND</td>
<td>39</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>39</td>
</tr>
<tr>
<td>2.2 Objectives</td>
<td>46</td>
</tr>
<tr>
<td>CHAPTER THREE. COMBUSTION AND SAMPLING SYSTEM</td>
<td>48</td>
</tr>
<tr>
<td>3.1 Combustion Furnace</td>
<td>49</td>
</tr>
<tr>
<td>3.2 Feeder System</td>
<td>51</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.3 Collection Probe</td>
<td>54</td>
</tr>
<tr>
<td>3.4 Cascade Impactor</td>
<td>56</td>
</tr>
<tr>
<td>4.1 Transmission Electron Microscope</td>
<td>62</td>
</tr>
<tr>
<td>4.2 Automated Image Analyzer</td>
<td>66</td>
</tr>
<tr>
<td>4.3 Mobility Classifier</td>
<td>66</td>
</tr>
<tr>
<td>4.4 Bulk Analysis</td>
<td>67</td>
</tr>
<tr>
<td>4.5 Scanning Transmission Electron Microscope</td>
<td>69</td>
</tr>
<tr>
<td>4.6 Auger Spectroscopy</td>
<td>93</td>
</tr>
<tr>
<td>4.7 ESCA</td>
<td>103</td>
</tr>
<tr>
<td>5.1 Fly Ash Mass Distribution</td>
<td>110</td>
</tr>
<tr>
<td>5.2 Bulk Chemical Composition</td>
<td>120</td>
</tr>
<tr>
<td>5.3 Combustion Temperature Time History</td>
<td>126</td>
</tr>
<tr>
<td>5.4 Vaporization</td>
<td>134</td>
</tr>
<tr>
<td>6.1 Bulk Composition</td>
<td>147</td>
</tr>
<tr>
<td>6.2 Dependence of Concentration on Particle Size</td>
<td>149</td>
</tr>
<tr>
<td>6.3 Surface Enrichment</td>
<td>156</td>
</tr>
<tr>
<td>6.4 Chemical State Analysis</td>
<td>165</td>
</tr>
<tr>
<td>7.1 Nucleation</td>
<td>179</td>
</tr>
<tr>
<td>7.2 Coagulation</td>
<td>193</td>
</tr>
<tr>
<td>7.3 Heterogeneous Condensation</td>
<td>209</td>
</tr>
<tr>
<td>7.3.1 Refractory Oxides</td>
<td>212</td>
</tr>
</tbody>
</table>
7.3.2 Volatile and Trace Species ........ 217

CHAPTER EIGHT. CONCLUSIONS AND RECOMMENDATIONS ........ 240

8.1 Conclusions ...................... 241

8.2 Recommendations ................. 244

REFERENCES .................................. 246
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Elemental Concentration for Primary Particles by STEM Verses Inverse Diameter</td>
<td>8</td>
</tr>
<tr>
<td>1.2</td>
<td>Concentration of Various Elements in the size Classified Fume Verses Inverse Diameter</td>
<td>9</td>
</tr>
<tr>
<td>1.3</td>
<td>Model Prediction for the Supersaturation of Magnesium Oxide</td>
<td>20</td>
</tr>
<tr>
<td>1.4</td>
<td>Experimental and Predicted Time Dependence for the Mean Diameter of the Primary Submicron Particles</td>
<td>22</td>
</tr>
<tr>
<td>1.5</td>
<td>Predicted Coalescence Time for Crystalline Magnesium Oxide Particles</td>
<td>24</td>
</tr>
<tr>
<td>1.6</td>
<td>Tendency for Critical Supersaturation of Sodium Sulfate as Combustion Products are Cooled in the Presence of Residual and Submicron Particles</td>
<td>31</td>
</tr>
<tr>
<td>1.7</td>
<td>Concentration of Sodium in the Residual Fly Ash Verses Inverse Diameter Squared</td>
<td>34</td>
</tr>
<tr>
<td>1.8</td>
<td>Fraction of Sodium Collected With the Fume for Various Degrees of Vaporization of the Total Ash</td>
<td>36</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic Diagram of Fly Ash Formation During Pulverized Coal Combustion</td>
<td>43</td>
</tr>
<tr>
<td>2.2</td>
<td>Fly Ash Particle Size Distribution Obtained From a Utility Boiler</td>
<td>45</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic Diagram of Laminar Flow Furnace</td>
<td>50</td>
</tr>
<tr>
<td>3.2</td>
<td>Gas Temperature Profiles in Laminar Flow Furnace</td>
<td>52</td>
</tr>
<tr>
<td>3.3</td>
<td>Schematic Diagram of Coal Feeder</td>
<td>53</td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic Diagram of Water Cooled Collection Probe</td>
<td>55</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic Diagram Showing Two Stages of a Cascade Impactor</td>
<td>57</td>
</tr>
<tr>
<td>4.1</td>
<td>Calibration of the Mobility Classifier With Respect to Primary Particile Diameter</td>
<td>68</td>
</tr>
<tr>
<td>4.2</td>
<td>Decay in Beam Current and Specimen Count Rate</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>With Time</td>
<td>74</td>
<td></td>
</tr>
<tr>
<td>4.3 STEM X-Ray Spectra Before (A) and After (B)</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Modifying the Aperature Configuration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.4 Adsorption Correction for Various Particle Diameters</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>4.5 Beam Broadening for Various PArticle Diameters</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>4.6 STEM Sensitivity Correction Factors Referenced to Sulfur</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>4.7 Auger Peak Amplitude Verses Beam Current</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>4.8 Auger Peak Amplitude Verses Sensitivity Settings</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>4.9 Auger Peak Amplitude Verses Modulation Amplitude Setting</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>4.10 Auger Spectra of Mg and MgO</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>4.11 ESCA High Resolution Scan of Carbon C 1s Line for Fume Sample</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>5.1 Mass Distribution of Particle Combustion Products on Cascade Impactor Stages and Final Filter</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>5.2 Distribution of Particulate Combustion Products</td>
<td>114</td>
<td></td>
</tr>
<tr>
<td>5.3 Fume Particles Produced From the Combustion of Montana Lignite in 40 (A) 20 (B) and 10 (C) Percent Oxygen in Nitrogen.</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>5.4 Volume-Mean Diameter of Submicron Primary Particles for Various Oxygen Partial Pressure</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>5.5 Particle Size Distribution of Particulate Combustion Products</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>5.6 Variation of Composition of the Fume for Various Combustion Conditions</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>5.7 Sulfur Retention in the Fume</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>5.8 Comparison of S to Na and K in the Fume</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>5.9 Average Particle Temperature of Montana Lignite (90/105 um) by Two Color Pyrometry</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>5.10 Buring Time for Montana Lignite (90/105 um)</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.11</td>
<td>Reciprocal of Burning Time Versus Ln(1 + Xo2)</td>
<td>133</td>
</tr>
<tr>
<td>5.12</td>
<td>Dependence on Oxygen Partial Pressure of Elemental and Ash Fraction in Fume</td>
<td>135</td>
</tr>
<tr>
<td>5.13</td>
<td>Variation of Elemental Mass Fraction with Particle Size for the Residual Fly Ash</td>
<td>137</td>
</tr>
<tr>
<td>5.14</td>
<td>Concentration of As in Size Classified Residual Fly Ash Particles</td>
<td>139</td>
</tr>
<tr>
<td>5.15</td>
<td>Temperature Dependence of the Elemental Vaporization Rates</td>
<td>142</td>
</tr>
<tr>
<td>5.16</td>
<td>Time Resolved Profile of Maximum Char Yield of Char and Submicron Particle Constituents</td>
<td>143</td>
</tr>
<tr>
<td>5.17</td>
<td>Time Resolved Measurement of the Mean Primary Particle Radius for the Submicron Particles</td>
<td>145</td>
</tr>
<tr>
<td>6.1</td>
<td>Elemental Concentration for Size Classified Samples by INAA</td>
<td>151</td>
</tr>
<tr>
<td>6.2</td>
<td>Elemental Concentration for Size Classified Samples by INAA</td>
<td>152</td>
</tr>
<tr>
<td>6.3</td>
<td>Elemental Concentration for Primary Particle by STEM</td>
<td>153</td>
</tr>
<tr>
<td>6.4</td>
<td>Sectioned Particle Showing the Contribution from the Outer Surface (A) and the Shaded Regions from the Ion Sputtering Gun</td>
<td>160</td>
</tr>
<tr>
<td>6.5</td>
<td>Escape Depth of Auger Electron Versus Electron Energy</td>
<td>162</td>
</tr>
<tr>
<td>6.6</td>
<td>ESCA High Energy Scan of Carbon C 1s Line for the Fume</td>
<td>166</td>
</tr>
<tr>
<td>6.7</td>
<td>ESCA High Resolution Scan of Magnesium Mg 2p line for the Fume</td>
<td>168</td>
</tr>
<tr>
<td>6.8</td>
<td>X-Ray Diffraction Lines for Submicron Particles</td>
<td>169</td>
</tr>
<tr>
<td>6.9</td>
<td>ESCA High Resolution Scan for Iron Fe 2p Line for the Fume</td>
<td>170</td>
</tr>
<tr>
<td>6.10</td>
<td>ESCA High Resolution Scan of Silicon Si 2p line for the Fume</td>
<td>172</td>
</tr>
<tr>
<td>6.11</td>
<td>ESCA High Resolution Scan of Sulfur S 2p line for the Fume</td>
<td>173</td>
</tr>
</tbody>
</table>
6.12 ESCA High Resolution Scan of Sodium Na 1s line for the Fume. 

6.13 ESCA High Resolution Scan of Calcium Ca 2p Line for the Fume. 

7.1 Equilibrium Vapor Pressure for Magnesium for Various Fuel Equivalence Ratio. 

7.2 Schematic Diagram of Magnesium Vaporization and Recondensation During Char Combustion. 

7.3 Model Prediction for the Supersaturation and Condensation of Magnesium. 

7.4 Primary Particle Size Distribution for the Fume with the Self-Preserving Size Distribution. 

7.5 Experimental and Predicted Growth of the Primary Submicron Particles. 

7.6 Predicted Coalescence Time for Solid Crystalline Magnesium Oxide Particles. 

7.7 Variation of Mean Diameter of Primary Submicron Particle with Degree of Vaporization of the Ash. 

7.8 Experimental and Predicted Growth of the Primary Submicron Particles. 

7.9 Profile of Silicon at Various Distances from Char. 

7.10 Elemental Concentration for Primary Particle by STEM Verses Inverse Diameter. 

7.11 Tendency for Critical Supersaturation of Sodium Sulfate as Combustion Products are Cooled in the Presence of Residual and Submicron Particles. 

7.12 Concentration of Various Elements in the Size Classified Fume Verses Inverse Diameter. 

7.13 Concentration of Na and K in the residual Fly Ash Verses Inverse Diameter Squared. 

7.14 Concentration of As and Sb in the Residual Fly Ash Verses Inverse Diameter. 

7.15 Superficial Area of Fume with Predictions from Self-Preserving Size Distribution. 

7.16 Fraction of Sodium Collected With the Fume for
Various Degrees of Vaporization of the Total Ash. . 234

7.17 Concentration of Na in the Residual Fly Ash Verses Inverse Diameter Squared . . . . . . . . . . . 235

7.18 Fraction of As and Sb Collected With the Fume for Various Degrees of Vaporization of the Total Ash. . 239
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Analytical Instruments Used for the Physico-Chemical Characterization of the Submicron Particles</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Auger Spectroscopy of the Fume Before and After Sputtering</td>
<td>11</td>
</tr>
<tr>
<td>1.3 Ratio of High and Low Energy Auger Electron Emission from the Submicron Particles and Homogeneous Bulk Standard</td>
<td>13</td>
</tr>
<tr>
<td>1.4 Mean Composition for 100 Coals</td>
<td>41</td>
</tr>
<tr>
<td>3.1 Calibration of the Ambient Andersen Impactor</td>
<td>59</td>
</tr>
<tr>
<td>3.2 Elemental Material Balance on Furnace and Collection System</td>
<td>61</td>
</tr>
<tr>
<td>4.1 Analytical Instrumentation Used for Physico-Chemical Characterization of the Submicron Particles</td>
<td>63</td>
</tr>
<tr>
<td>4.2 Calibration of the Magnification Settings for the Philips 200 TEM</td>
<td>65</td>
</tr>
<tr>
<td>4.3 INAA Analysis of Opel Glass, NBS Standard Number 91</td>
<td>70</td>
</tr>
<tr>
<td>4.4 Sources of Error and Correction Implimented in Order to Obtain Quantitative X-Ray Analysis of the Submicron Particles with the STEM</td>
<td>72</td>
</tr>
<tr>
<td>4.5 Repetitive Analysis of Submiron Particles for the Elements Silicon and Iron</td>
<td>77</td>
</tr>
<tr>
<td>4.6 Theoretical and Experimentally Determined Sensitivity Correction Factors for 100 Kv</td>
<td>88</td>
</tr>
<tr>
<td>4.7 Comparison of the Chemical Analysis by the STEM and Neutron Activation (INAA)</td>
<td>90</td>
</tr>
<tr>
<td>4.8 Elemental Retention During Analysis with the High Intensity Electron Beam of the STEM</td>
<td>92</td>
</tr>
<tr>
<td>4.9 Relative Sensitivity Factors Obtained Experimentally (Ep = 5.0 Kev)</td>
<td>102</td>
</tr>
<tr>
<td>4.10 Calibration of ESCA Spectrometer with Au, Ag,</td>
<td></td>
</tr>
</tbody>
</table>
4.11 Comparison of the Peak Position from Standards with the Reference Binding Energy Compiled by PHI .......................................................... 108

5.1 Coal Composition for Major, Minor, and Trace Elements ................................................................. 124

5.2 Submicron Fume Composition ......................................................... 125

6.1 Chemical Analysis of the Submicron Particles Produced from the Combustion of Montana Lignite (45/53 um) at Furnace Temperature of 1700 K in Twenty Percent Oxygen in Nitrogen .................................................. 149

6.2 STEM Microprobe Analysis of Individual Submicron Particles Produced from the Combustion of Montana Lignite (150 um) at Furnace Temperature of 1700 K in Seventy Five Percent Oxygen ............................................... 155

6.3 Auger Spectroscopy of the Fume Produced from the Combustion of Montana Lignite (45/53 um) at a Furnace Temperature of 1700 K in Twenty Percent Oxygen in Nitrogen .................................................. 157

6.4 Auger Spectroscopy of the Fume Before and After Sputtering .................................................................. 159

6.5 Ratio of High and Low Energy Auger Electron Emission from the Submicron Particles and Homogeneous Bulk Standard .................................................. 163

and Cu Metal Standards .................................................................................................................. 107
1.1 INTRODUCTION

Interest in the control of fine particles emitted by coal combustion is motivated by environmental considerations since fine particles can penetrate deep into the lungs and contain a relatively high concentration of toxic trace species. Studies of size distribution of the ash emitted by utility boilers (Markowski et al., 1980) shows that most of the ash is concentrated in a size range of 1 to 20 microns but that a small amount, of the order of one percent of the total ash by weight, is present in the submicron size range which shows up as a distinct spike in the particle size distribution. The mechanisms for the formation of the ash in the two size ranges are different. The larger particles are produced by the fusion and coalescence of mineral matter in coal (Padia, 1976). The finer particles, in the submicron size range, are produced by the vaporization and condensation of the mineral constituents (Flagan, 1979). Studies of the composition of larger ash particles have shown that these have concentrations of volatile trace species that increase with decreasing particle size (Davison et al., 1974) and that the surface layers of the particles are enriched in the
same trace species (Linton et. al., 1977). This is consistent with a hypothesis that trace metal vapors condense on the surface of the residual ash particles produced during coal combustion with the rate of deposition being controlled by mass transfer (Flagan and Friedlander, 1978).

In general, the toxic effects of the fine particulates (i.e., submicron) are unknown because field data pertaining to their physico-chemical characteristics are fragmentary, and relevant toxicological experiments have not yet been conducted. The objectives of this thesis are to determine the physico-chemical characteristics of the submicron particles under simulated pulverized coal combustion conditions and to obtain a better understanding about the evolution of these particles with particular emphasis on the sequence of condensation for the vaporized inorganic elements and the distribution of the volatile and trace species between the two size modes.

1.2 EXPERIMENTAL APPARATUS

A dilute cloud of coal particles is burned under well controlled, reproducible conditions in a laminar flow furnace. Small homogeneous samples of well size classified coal particles are fed through a narrow water cooled feeder tube and are injected axially into a preheated oxygen/nitrogen mixture. The coal particles heat up rapidly, ignite, and burn in a narrow stream within $6.2 \times 10^{-3}$ meters
of the center axis, where radial dispersion of the particles is minimized by the stable laminar flow field.

All the combustion products, both gaseous and solid, are collected at a specified distance from the point of coal injection in the furnace by a water cooled probe whose position may be adjusted in order to vary residence time. At the entrance to the probe, the combustion products are rapidly quenched and diluted. Particle deposition within the probe is avoided by transpiring gas through a porous liner in the probe. The particles and gas from the collection probe are passed through an Andersen Impactor for on-line aerodynamic size classification of the particles greater than 0.3 μm. The submicron particles, because of their small size, pass through the impactor. Several collection procedures were utilized for these submicron particles depending upon the information sought. Collection on 0.2 μm fluoropore filter was utilized for weight and chemical analysis, deposition on transmission electron microscope grids placed in an electrostatic precipitator for microscopy studies, or on-line size classification using a mobility classifier (Knutson et. al., 1975) for measurement of the variation in composition with particle size.

Insight on the fundamental processes governing the formation of the submicron aerosol can be obtained from detailed physico-chemical characterization of the submicron particles. A list of the analytical techniques employed for
the characterization of submicron particles is presented in Table 1.1. Particle size distributions for the submicron particles are obtained from TEM micrographs by an automated image analyzer. The bulk elemental composition of the submicron particles is determined by instrumental neutron activation analysis (INAA), atomic adsorption (AA), and liquid chromatography (Mizisir et. al., 1978). The elemental composition of individual primary particles is obtained with a 100kv field emission scanning transmission electron microscope (STEM) fitted with an energy dispersive x-ray spectrometer (Vander Sande, 1979). Because of uncertainty in the adsorption characteristics of the detector, sensitivity correction factors for the light elements (Mg, Al, and Si) had to be determined. The unique feature of this system is its twenty angstrom spatial resolution for elemental analysis of single particles. However, under the high intensity electron beam the volatile species such as sulfur and potassium were preferentially lost during analysis. Consequently, analysis by this method is limited to the stable elements: silicon, iron, calcium, and magnesium, the x-ray signals of which remain constant during exposure to the high intensity electron beam. Auger spectroscopy is used to obtain information about the elemental stratification within the submicron particles. The depth of analysis is determined by the mean free path of the Auger electron which is a function of elemental composition and is of the order of twenty angstroms. The instrument used was a PHI 590A scanning Auger
Table 1.1 - Analytical instrumentation used for physicochemical characterization of the submicron particles

<table>
<thead>
<tr>
<th>INSTRUMENT</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical Characterization</strong></td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>Particle morphology</td>
</tr>
<tr>
<td>Automated image analyzer</td>
<td>PSD</td>
</tr>
<tr>
<td>Mobility classifier</td>
<td>Discrete sized Samples within the submicron mode</td>
</tr>
<tr>
<td><strong>Chemical Characterization</strong></td>
<td></td>
</tr>
<tr>
<td>INAA, AA, and liquid chromatography</td>
<td>Bulk analysis</td>
</tr>
<tr>
<td>STEM</td>
<td>Individual particle analysis</td>
</tr>
<tr>
<td>AUGER spectroscopy</td>
<td>Surface analysis</td>
</tr>
<tr>
<td>ESCA, mossbauer, and x-ray diffraction</td>
<td>Chemical state</td>
</tr>
</tbody>
</table>
microprobe with submicron spatial resolution of two tenths of a micron for analysis. The 590A utilizes both single pass electron optics for image analysis and an argon ion sputtering gun for depth profiling. Relative sensitivity factors had to be redetermined for the specific compounds found in the fume since the peak to peak amplitude of the differential signal was found to be sensitive to the chemical state for some of the elements. In order to minimize severe charging under the incident electron beam in Auger analysis, a conductive silver membrane filter was employed for the collection of the submicron particles.

1.3 RESULTS

For carefully controlled combustion conditions, the important variables which govern the physico-chemical characteristics of the submicron particles (i.e., size, amount, and bulk composition) were examined. The details have been presented elsewhere (Neville et. al., 1980; Haynes et. al., 1981; Quann, 1982). The results presented here will focus in detail on the chemical characteristics of the individual submicron particles produced from the combustion of Montana lignite 45/53 μm in twenty percent oxygen in nitrogen.

1.3.1 Dependence of concentration on particle size

Data were obtained by two methods. A STEM was used to analyze individual particles and INAA was used to analyze size segregated particles collected and sized by a mobility
Particles with diameters ranging between 80 and 400 angstroms were analyzed at random using the STEM. The elemental concentration of individual particles versus reciprocal diameter is plotted in Figure 1.1. The concentration of Mg, Ca, and Fe show no major trend with particle size whereas silicon exhibits a marked increase in concentration with decreasing particle size.

Four discrete cuts of the submicron particles obtained from the mobility classifier with mean particles diameters of 100, 200, 300, and 400 angstroms were analyzed by INAA. The relative concentration of Mg, Fe, Ca, Na, As, and Sb are reported in Figure 1.2. These results show a systematic increase in concentration with decreasing particle size for all elements other than Mg, Ca, and Fe. The concentrations of iron, calcium, and magnesium did not vary with particle size in either the STEM analysis of individual particles or the INAA analysis of size classified samples.

1.3.2 Surface Enrichment

The enrichment of the particle's surface in selected elements was determined by: (1) comparing the surface concentration, measured by Auger spectroscopy, with the bulk concentration measured by INAA, AA, and liquid chromatography; (2) determining the variation in concentration measured by Auger spectroscopy as the surface layers
Figure 1.1 - Elemental concentration for primary particles by STEM versus inverse diameter.
Figure 1.2 - Concentration of various elements in the size classified fume versus inverse diameter

MOBILITY CLASSIFIER

- Na $\times 1.0E\ 1$
- As $\times 4.8E\ 3$
- Sb $\times 2.8E\ 4$
- Ca
- Mg $\times 2.8E\ -1$
- Fe
were sputtered away; and (3) comparing the ratio of the intensity of the high and low energy Auger electrons emitted from the sample to the ratio for a homogeneous bulk standard.

The surface concentration measured by Auger electron spectroscopy (column one) is compared in Table 1.2 with the bulk particle concentration by INAA ($\text{Na}_2\text{O}$, $\text{CaO}$, $\text{MgO}$, $\text{FeO}$), AA ($\text{K}_2\text{O}$, $\text{SiO}_2$), and liquid chromatography ($\text{SO}_3$) (column four). All elements are reported as their oxides for convenience. A comparison of the two analyses shows that sodium, sulfur, potassium, and silicon are highly concentrated in the surface layers, while magnesium and iron are depleted. From the comparison of the two analysis, calcium is neither highly enriched nor depleted in the surface layers.

In order to obtain the concentration as a function of depth from the surface, the fume sample was sputtered at a milling rate that corresponds to a surface regression rate of about twenty five angstroms per minute for a $\text{Te}_2\text{O}_5$ sputtering standard (Martin, 1981). Auger analyses of the original surface and at several sputtered times are presented in Table 1.2. The concentration of species in which the surface is enriched, such as that of sodium, sulfur, and potassium, decrease as the surface layers are sputtered away, while species in which the surface is depleted, such as magnesium and iron, increase. The relative concentration of calcium with successive sputtering remains constant suggesting that calcium is present near the surface as well as in the core of
Table 1.2 Auger spectroscopy of the fume before and after sputtering.

<table>
<thead>
<tr>
<th>species</th>
<th>surface conc. (wt%)</th>
<th>sputter 1 minute (wt%)</th>
<th>sputter 3 minute (wt%)</th>
<th>bulk conc. (INAA)* (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>11.8</td>
<td>6.0</td>
<td>4.6</td>
<td>5.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.6</td>
<td>3.7</td>
<td>1.8</td>
<td>7.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>16.4</td>
<td>6.4</td>
<td>3.5</td>
<td>1.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.9</td>
<td>13.3</td>
<td>13.8</td>
<td>3.3</td>
</tr>
<tr>
<td>CaO</td>
<td>12.3</td>
<td>11.3</td>
<td>11.7</td>
<td>9.7</td>
</tr>
<tr>
<td>MgO</td>
<td>29.3</td>
<td>49.1</td>
<td>53.1</td>
<td>58.6</td>
</tr>
<tr>
<td>FeO</td>
<td>3.9</td>
<td>6.5</td>
<td>7.8</td>
<td>11.8</td>
</tr>
</tbody>
</table>

* supplemented with AA and liquid chromatography
the particle. It should be noted that the sputtering rate is uniform over a horizontal cross-section and that the Auger emission for a sectioned particle will always include contributions from surface layers.

Another measure of the elemental stratification within the submicron particle is provided by a comparison of intensities from the KLL and LMM Auger emission for specific elements in the fume with those from a homogeneous bulk standard (Kane, 1974; King, 1979). The extent of attenuation of the Auger electron moving through a solid will be highly dependent on its own mean free path. The escape depth (or mean free path $\lambda$) of the low energy LMM Auger electrons (~100 ev) is considerably smaller than that of the high energy KLL Auger electrons (~1000 ev). Consequently, the ratio of the intensity of the high energy to the low energy Auger emission for a subsurface element, relative to the ratio obtained from a homogeneous bulk standard, will increase as the distance of the elements from the surface increases. Therefore, a comparison of the intensity ratios for the elements in the submicron particles with those from homogeneous bulk standard provides a measure of the distribution of sulfur, magnesium, and silicon as a function of depth (see Table 1.3). For sulfur, the ratio is close to, but slightly greater than, the ratio from the homogeneous bulk sample, which suggests that sulfur is in the outer surface layer of the submicron particle. For magnesium, the intensity ratio
### Table 1.3 Ratio of high and low energy Auger electron emission from the submicron particles and homogeneous bulk standards

<table>
<thead>
<tr>
<th>element</th>
<th>electron energy</th>
<th>$\lambda$ A°</th>
<th>fume ratio</th>
<th>standard ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>120</td>
<td>4</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>S</td>
<td>1834</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>76</td>
<td>4</td>
<td></td>
<td>10.4</td>
</tr>
<tr>
<td>Si</td>
<td>1606</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>35</td>
<td>6</td>
<td></td>
<td>54</td>
</tr>
<tr>
<td>Mg</td>
<td>1190</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
greatly exceeds that ratio from the homogeneous standard suggesting that magnesium is in the core of the particle. The extent of attenuation of the low energy emission for silicon indicates that this element lies between the outer surface layer enriched in elements such as sulfur and the particle's core enriched in elements such as magnesium.

The above data are only semi-quantitative because of complexities introduced by the different degrees of attenuation for the Auger electrons emitted by different elements and because of the averaging of the emissions from different chords in a spherical particle. The results are further complicated by the attenuation of the Auger electrons by a carbon film that forms on the sample's surface. The results in Table 1.2 suggest that silicon is in the surface layer whereas those in Table 1.3 suggest it is in an intermediate layer. This apparent anomaly is explained by the larger mean free path of silicon KLL auger electron (25 angstroms) compared to that of sulfur (4.3 angstroms). The adsorbed carbon contamination present on the outer surface of the sample will attenuate the sulfur signal to a greater extent than the attenuation of the silicon signal by surface layers. Therefore, Auger analysis yields an apparently high silicon surface concentration. However, by the use of several measurement techniques such as those employed in this study, a coherent story can be developed.
1.4 DISCUSSION

The elemental stratification within the submicron particle provides a record of the condensation sequence for the various inorganic vapors. The elements present in the core of the submicron particles (i.e., Mg, Ca, and Fe) are believed to be responsible for the formation of the initial condensed phase by homogeneous nucleation, while those elements such as Na and K which form the outer layers of the submicron particles are believed to condense at much lower temperatures. The phenomena involving the initial formation of the submicron particles should be evident by examining the vaporization and condensation of magnesium, which not only resides in the core of the submicron particles, but also accounts for over sixty percent of the submicron particle by weight.

1.4.1 Particle Nucleation

From the rate of vaporization of different compounds it is possible to infer their partial pressure at the surface of the burning char particle. For magnesium, the vapor pressure calculated from the rate of vaporization, was found to exceed the equilibrium vapor pressure for magnesium oxide by several orders of magnitude (Quann, 1982). The high rate of vaporization is explained by chemical reduction of the oxide to the more volatile metal vapor in the locally reducing atmosphere within a burning char particle. The metal
vapors will reoxidize as they diffuse away from the burning char particle into the surrounding oxidizing environment. Upon reoxidation, the oxide vapors will be supersaturated, thus providing the necessary driving force for homogeneous nucleation. The decrease in temperature away from the particle can only accentuate this tendency.

A steady state model was developed in order to examine in detail the phenomena involving the homogeneous nucleation of magnesium oxide. The model estimates the temperature, oxygen partial pressure, magnesium metal partial pressure, and magnesium oxide partial pressure from the governing differential equations as a function of distance from the char particle. The temperature at various distances from the char particle was derived from Fourier's law of heat conduction

$$\frac{1}{r^2} \left( \frac{d}{dr} \left( r^2 k \frac{dT}{dr} \right) \right) = 0$$

Eq. 1.1

where the particle temperature was determined by two color pyrometry (Timothy et. al., 1980). The oxygen partial pressure at various distances from the char particle was derived from Fick's first law,

$$\frac{1}{r^2} \left( \frac{d}{dr} \left( r^2 D_{AB} \frac{dn_{O_2}}{dr} \right) \right) = 0$$

Eq. 1.2

where the oxygen partial pressure at the surface of the char particle was calculated from char oxidation kinetics (Field,
1967). The partial pressure of magnesium at various distances from the char particle was governed by the differential equation,

$$\frac{1}{r^2} \left( \frac{d}{dr} \left( r^2 D_{AB} \frac{dn_{Mg}}{dr} \right) \right) = -K_{n_{Mg} n_{O_2}}$$  \hspace{1cm} \text{Eq. 1.3}$$

where the magnesium partial pressure at the surface of the char particle was calculated from experimental vaporization data (Quann, 1982). The reaction term, $-K_{n_{Mg} n_{O_2}}$, accounts for the consumption of magnesium metal vapor by oxidation. The modeling of the homogeneous gas phase oxidation of magnesium will entail establishing the rate coefficient for the governing bimolecular reaction

$$\text{Mg}(v) + \text{O}_2 \longrightarrow \text{MgO}(v) + \text{O}$$  \hspace{1cm} \text{Eq. 1.4}$$
as proposed by Markstein (1963). The low pressure, low temperature studies concluded that the bimolecular homogeneous reaction will account for initial formation of magnesium oxide vapors which, upon supersaturation, will homogeneously nucleate to form the initial particles. For the atmospheric high temperature environment of combustion, the estimated rate coefficient from collision theory was used to model the bimolecular oxidation of magnesium metal vapors (Laider, 1965).

The partial pressure of magnesium oxide at various distances from the char surface was governed by the differen-
tial Equation,

\[
\frac{1}{r^2} \left( \frac{d}{dr} \frac{r^2 D_{AB}}{d} \frac{dn_{MgO}}{dr} \right) = R_{\text{Rxn}} + R_{\text{Nucl}} + R_{\text{Het}} \quad \text{Eq. 1.6}
\]

\[
R_{\text{Rxn}} = K n_{Mg}^3 n_{O_2}^1
\]

\[
R_{\text{Nucl}} = I \left( \frac{r^*}{r_m} \right) \left( \frac{1}{N_{av}} \right)
\]

\[
R_{\text{Het}} = F'_i(d) \left( \frac{N}{N_{av}} \right)
\]

where the reaction terms on the right hand side of equation 1.6 account for the continual production of magnesium oxide vapors by oxidation of the metal vapors, \( R_{\text{Rxn}} \), the consumption of magnesium oxide by homogeneous nucleation, \( R_{\text{Nucl}} \), and the consumption of magnesium oxide vapors by heterogeneous condensation on the stable nuclei of magnesium oxide. The rate of homogeneous nucleation of a spherical liquid droplet for single component vapors, \( I \), was calculated from the classical theory of nucleation of Volmer and Weber and Becker and Doering (Hirth et. al., 1963) using the predicted magnesium oxide partial pressure and equilibrium vapor pressure. The size of the stable nuclei forming by homogeneous nucleation is specified by the critical cluster size, \( r^* \), which is a cluster of size such that the addition of one monomer will lead to the formation of a stable cluster. The rate of heterogeneous condensation of the condensable vapors is determined from the rate of deposition per particle for free molecular regime (\( Kn >> 10 \)) which is derived from the kinetic theory of gases (Friedlander, 1977) and the number density, \( N \), for the stable nuclei formed by homogeneous-
ous nucleation. In assuming a nearly monodisperse particle size distribution, a simple solution to the kinetic equation for brownian coagulation can be used to approximate the rate of change in the number density and average particle size of the stable nuclei as a result of coagulation.

The model's predictions for the condensation of magnesium corresponding to the combustion condition for Montana lignite in twenty percent oxygen in nitrogen are presented in Figure 1.3. The supersaturation of magnesium oxide is predicted to occur within the thermal boundary layer of the char particle due to the relatively high rate for the homogeneous oxidation of magnesium. The model predicts a very sharp rise in the nucleation rate as supersaturation increases. This position is relatively insensitive to uncertainties in the assumed values for the oxidation rate constant of Mg(v) and MgO surface tension (Smithells, 1965), and the estimate of the magnesium oxide and oxygen partial pressures at the char particle's surface. Since the onset of nucleation is very sensitive to temperature, changes in the values assumed for the above parameters will result in only a slight displacement of the position for the onset of nucleation because of the steepness of the temperature gradient near the particle surface. The duration of the nucleation wave is attributed to the continual addition of monomer by homogeneous gas phase oxidation of magnesium metal vapor. Since the transient time for establishing the steady state
Figure 1.3 - Model prediction for the supersaturation of magnesium oxide
gas and temperature profiles around the char particle is extremely short and the fact that the characteristic times for oxidation and nucleation are over two orders of magnitude shorter than the time for char burnout, magnesium can be assumed to homogeneously nucleate very early on during the combustion process, where the temperature is relatively high.

1.4.2 PARTICLE GROWTH

The classical nucleation theory predicts the formation of a large number of particles (a nucleation rate of $1.0 \times 10^{17}$ nuclei/cc sec) of extremely small size. Due to an initially high particle number density, the particles will grow rapidly. The studies of the growth of inorganic particles of SiO$_2$ (Ulrich et al., 1976), Pb (Graham and Homer, 1973), and soot (Wagner, 1979) have been shown to be well governed by coagulation theory. In the present study the theory was shown to apply to the inorganic submicron particles produced from simulated pulverized coal combustion where the rate of coagulation was governed by the collision frequency of the particles due to random Brownian motion and that particle coalescence was assumed to occur instantaneously to form single spherical particles upon contact. The experimentally measured mean particle diameter at various distances from the point of coal injection are compared with the predictions from coagulation theory in Figure 1.4. The particle size distribution is found to be in good agreement with the self preserving distribution function (Friedlander,
Figure 1.4 - Experimental and predicted time dependence for the mean diameter of the primary submicron particles
1977). For early growth periods the coagulation theory provides an excellent representation of the change in primary particle size with time. From extrapolation of the growth curve, it is apparent that the formation of the submicron particles is occurring at the initiation of char combustion. The continuous addition of new material due to further vaporization during char combustion is accommodated by adjustment in the volume fraction. In examining the growth curve in Figure 1.4 the primary particle growth ceases shortly after char burnout as the gas temperature drops back down to the furnace gas temperature of 1700 K and as the particle diameter approaches 160 angstroms. This apparent break between theory and experimental observation can be explained by a decrease in coalescence rate. The time for coalescence, governed by solid-state diffusion for two particles having the same diameter may be estimated from the relationship

\[ t = \left[ \frac{\Delta L \left( \sqrt{2} \frac{K}{T} \right) r^{6/5}}{L_0 \left( 20 a^3 D^* \right)} \right]^{5/2} \]  

Eq. 1.7

where \( \Delta L/L_0 \) is the fractional shrinkage of the coalescing particles, \( a^3 \) is atomic volume of diffusing vacancy, and \( D^* \) is the self diffusion coefficient (Kingery, 1965). A solid phase diffusion coefficient for crystalline magnesium oxide was selected to derive estimates of coalescence times in Figure 1.5. The decrease in temperature on completion of combustion and the increase in particle diameter both contribute to the decrease of the coalescence rate. The primary
Figure 1.5 - Predicted coalescence time for crystalline magnesium oxide particles
particle diameter is in the range of 120 to 160 angstroms when both these factors become important. Beyond this point, further coagulation leads to the formation of agglomerated particles where the discrete size of the colliding particles is conserved. The projected areas of the agglomerated particles at a sampling position of 20 cm from the point of injection of the coal is in very good agreement with the coagulation theory. The fact that the coalescence of these particles ceases at relatively high temperatures (i.e. 1700 K) is consistent with the hypothesis that the species Na, S, and K condense at much lower temperatures as the combustion products are being cooled since these impurities would undoubtedly increase the coalescence rate at 1700 K (Kingery, 1965).

1.4.3 CONDENSATION

In a manner analogous to magnesium, the vaporization of calcium, iron, and, silicon is augmented by the chemical reduction of the refractory oxides to the more volatile suboxide vapor (SiO) and metal vapor (Ca and Fe) because of the locally reducing environment within the char particle. As these vapors diffuse into the oxidizing environment surrounding the char particle, they will reoxidize. The sequence of condensation for the various refractory species will be highly dependent on the rate coefficients for their oxidation and their relative partial pressures. Subsequent to the formation of stable nuclei, one might anticipate an
increase in the condensation rate by heterogeneous oxidation of the metal or suboxide vapors by collision with the oxygen atom layer formed on the surface of the growing particles. The contribution of this mechanism to MgO formation is estimated to be two orders of magnitude smaller than that due to homogeneous oxidation, even when neglecting the low collision efficiency of magnesium atoms with the surface at high temperatures (Markstein, 1969; Glassman, 1959).

Silicon condenses late relative to magnesium, calcium, and iron because the silicon concentration is low and its rate of oxidation is slow. The silicon monoxide vapor pressure at the surface is reduced to a level below the equilibrium value because of a diffusional resistance. Such a diffusional limitation is not important for magnesium and calcium because magnesium and calcium are finely dispersed in an elemental form in the original coal particle in contrast to silicon which is present in discrete mineral inclusions (Quann, 1982). The rate of oxidation of a monoxide such as SiO to SiO$_2$ is expected to be much slower than that of the oxidation of the metal to the monoxide; this statement is based on an analogy with aluminum for which it is found that the oxidation of aluminum by O$_2$ to AlO is two orders of magnitude faster than that of AlO to AlO$_2$ (Fontijn, 1976). The proximity of the saturation of calcium and iron to the surface of the burning char particle as determined from the steady state model suggests that these species like magnesium
condense shortly after the onset of char combustion. However, silicon is shown to saturate only as the local gas temperature drops back to the furnace temperature upon completion of the combustion of the char particles.

Since the submicron particles are smaller than the mean free path of the gas molecules, the rate of heterogeneous condensation of the vapor molecules on the particles will be governed by the frequency with which the condensable vapors collide with the surface of the particles. In the free molecular regime, the rate of heterogeneous condensation per particle, \( F_i(d) \), as calculated from the kinetic theory of gases (Friedlander, 1977) is given by

\[
F_i(d) = \frac{\pi d_p^2 (P_i - P_{eq,i})}{(2 \pi m k T)^{1/2}}
\]

Consequently, the concentration dependence of those species which condense heterogeneously on the surface of the submicron particles is predicted to be inversely proportional to particle diameter. From the STEM analysis of individual submicron particles, the concentration dependence for silicon is best correlated with inverse diameter, Figure 1.1, while the concentration of magnesium, calcium, and iron show no dependence on particle size. The interparticle concentration of those species which condense relatively early during the growth process should be relatively uniform since the evolution of the submicron particles will entail the coalescence of
a large number (i.e., $1.0 \times 10^4$) of various sized particles. However, in the case of silicon, the predicted particle size dependence is preserved since silicon condenses heterogeneously after the coalescence of the primary particles has ceased. The late condensation of silicon relative to the other refractory oxides is further supported by Auger spectroscopy which has shown silicon to be present near the outer surface of the submicron particles while magnesium, calcium, and iron are shown to make up the core of the submicron particles.

The volatile and trace species are assumed to condense at much lower temperatures than the refractory oxides of calcium, magnesium, iron, and silicon either because they are present in dilute quantities or have much higher vapor pressures than the refractory oxides. Whether these species condense heterogeneously or homogeneously will be highly dependent on the area of the residual and primary submicron particles available for heterogeneous condensation and the rate at which the combustion products are cooled.

The method employed for determining whether homogeneous nucleation of the volatile and trace species can occur in the presence of the pre-existing particles will be determined by establishing whether or not the criteria for homogeneous nucleation has been exceeded (i.e., $I = 1$ nuclei/cc sec) (Hirth et. al., 1963). As the combustion products are cooled the volatile and trace species will eventually saturate. As
the gases are cooled further, the partial pressure of species i will be determined by calculating the amount of the condensable vapor that condenses heterogeneously on the pre-existing particles over the short time increment at each temperature. The amount of condensable vapor species remaining in the gas phase after each step will be used as the starting amount for the next time increment at the next temperature. For diffusion-limited heterogeneous condensation, the amount of condensing volatiles will be determined from the flux integral \( \int n(v) F_i \, dv \). For the residual ash particle mode which obeys continuum behavior (Kn << 1), the particle size distribution function, \( n(v) \), is approximated numerically from the experimental data and the diffusion flux, \( F_i(d) \), which is given by

\[
F_i(d) = \frac{2 \pi \eta d \Delta P (P_i - P_{eq,i})}{kT} \quad \text{Eq. 1.9}
\]

For the submicron particle mode which exhibits free molecular behavior (i.e., Kn >> 10), the size distribution function \( n(v) \) is represented by self-preserving size distribution function, \( \Psi(\eta) \), and the molecular diffusion flux, \( F'_i(d) \), is obtained from equation 1.8. In establishing the flux of condensable vapors to the submicron particles, both the Kelvin effect (Friedlander, 1977) and the reduction in the area of the primary particles due to agglomeration (Medalin, 1967) will be taken into account.

The model's predictions for the extent of supersatur-
ation of sodium in the presence of the residual and submicron particles for various cooling rates are presented in Figure 1.6. For a low chlorine content coal such as Montana lignite, sodium sulfate is the thermodynamically favored vapor species over the temperature range at which the sodium is anticipated to condense (McNellan et. al., 1981). Furthermore, chemical state analysis by ESCA shows that sodium is present as sodium sulfate in the submicron particles. The equilibrium vapor pressure for sodium sulfate is calculated assuming a pure condensed phase. The particle size distribution for the residual and submicron particles is based on the fly ash distribution obtained from the combustion of Montana lignite 45/53 um at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen. The rate at which the combustion products are cooled as they approach the water cooled collection probe was estimated from the temperature profiles in the furnace to range between 2,000 K/sec to 7,000 K/sec. Assuming all the sodium vaporizes during combustion, the sodium vapors are predicted to saturate at about 1400 K. As the gases are cooled below 1400 K at a rate of 5,000 K/sec, all the sodium is predicted to condense heterogeneously. Only at much higher cooling rates, 40,000 K/sec, is the partial pressure of sodium predicted to exceed the critical supersaturation partial pressure necessary for the onset of homogeneous nucleation. However, even at a cooling rate of 40,000 K/sec, over ninety percent of the sodium is still predicted to condensed heterogeneously before
Figure 1.6 - Tendency for critical super saturation of Na$_2$SO$_4$ as combustion products are cooled in the presence of residual and submicron particles.
the criteria for homogeneous nucleation is satisfied. Like sodium, the other volatile and trace species are assumed to condense heterogeneously as the combustion products are cooled.

For diffusion-limited condensation the concentration dependence of those species which condense heterogeneously on the submicron particles have been shown to be inversely proportional to particle size. The concentration of Na, As, Sb, Fe, Ca, and Mg obtained from the INAA of discrete size classified samples of the submicron particles are plotted versus reciprocal diameter in Figure 1.2. The observation that the concentration dependence of As, Sb, and Na is best correlated by $d^{-1}$ relationship supports the model's prediction that the volatile and trace species condense heterogeneously as the gases are being cooled. The determination of the stratification of the various elements within the submicron particle by Auger spectroscopy show that the volatile species form the outer most surface of the submicron particle.

Under the combustion conditions examined, the volatile species had been previously assumed to totally vaporize during combustion due to their high volatility. However, based on the respective surface area of the two size modes the discrepancy between the amount of volatile species appearing in the submicron particles with that in the parent coal (i.e., ~ forty percent) cannot be explained by the
amount of material condensing on the residual fly ash particles since the submicron particles account for over ninety percent of the free area available for heterogeneous condensation. The concentration of sodium in the residual fly ash from the combustion of Montana lignite in 45/53 µm at a furnace temperature of 1700 K in twenty percent oxygen is shown in Figure 1.7 to be inversely proportional to diameter squared, which suggests that a substantial fraction of the sodium in the residual fly ash is present as a result of heterogeneous condensation. However, the fact that the intercept for the sodium concentration versus $1/d^2$ is positive also suggests that not all the sodium volatilized during combustion. From the concentration trend, about seventy percent of the sodium is estimated to vaporize. In order to explain the distribution of the vaporized sodium, the competition between the primary spheres of the fume and the residual fly ash particles as a sink for the condensing sodium vapors was examined for various degrees of ash vaporization, $\phi$. As the fraction of total ash vaporized is varied, the total area of the residual fly ash will remain relatively constant while the total area of the fume will vary by $\phi^{0.6}$ (i.e., self-preserving identity). For diffusion-limited condensation, the distribution of the volatile species between the two modes can be estimated from the flux integral for the residual fly ash particles and the primary spheres of the submicron particles. As previously stated, the Kelvin effect and the reduction in the area of
Figure 1.7 - Concentration of sodium in the residual fly ash versus inverse diameter squared
the primary particles due to agglomeration are taken into account in the flux integral for the submicron particles.

A comparison between the predicted and experimental fraction of sodium appearing in the fume for various degrees of ash vaporization is shown in Figure 1.8 where the amount of sodium vaporized was estimated from the concentration trends for each condition. The fraction of vaporized sodium appearing in the submicron particles (i.e., fume) is shown to be fairly well predicted by a cooling rate of 2,000 K/sec which is the lower bound for the cooling rate estimated in the furnace. The increase in the fraction of sodium appearing in the fume as the amount of total ash vaporized, $\phi$, is increased from less than one percent to over twenty percent can be attributed to the increase in the area of the fume by $\phi^{0.6}$. The variation in the prediction of sodium appearing in the fume with cooling rate can be attributed to the fact that at lower cooling rates the concentration of condensable vapor is shown to remain fairly close to the saturation vapor pressure (see Figure 1.7). Consequently, for low cooling rates, the potential for condensation, $(P_i - P_{eq,i})$, will be small enough that the Kelvin effect will preferentially reduce the potential for condensation to the submicron particles. However, as the cooling rate is increased the supersaturation of the condensable vapor increases and the Kelvin effect becomes less pronounced due to the increase in the potential for condensation.
Figure 1.8 - Fraction of sodium collected with the fume for various degrees of vaporization of the total ash.
1.5 CONCLUSION

The submicron inorganic particles produced during coal combustion have a stratified concentration. The inner core of the particles in the present study on a Montana lignite consists mainly of the oxides of magnesium, iron, and calcium produced by the vaporization of the metals generated in the locally reducing regime within a burning char particle, oxidation of the metal vapors and the homogeneous nucleation of the resulting oxides near the surface of the burning particle. The nuclei coagulate at a rate which is adequately predicted by classical coagulation theory. In the early stages of coagulation the particles coalesce, but, as the temperature in the vicinity of the particles decreases subsequent to the completion of combustion of the char and as the primary particle diameter increases, the coalescence rate decreases and the agglomerates produced appear as aggregates of spheres. Silicon monoxide generated in the locally reducing atmosphere of the burning char particle is oxidized to silica at a relatively slow rate and therefore condenses on the core produced by iron, calcium, and magnesium oxides. As the combustion products are cooled volatile compounds of metals such as Na, As, and Sb condense to produce the outer layer of the inorganic particles. The distribution of the volatile species between the two size modes is sensitive to the rate at which the combustion products are cooled and the fraction of the total ash vaporized. The hypotheses relating
to the condensation sequence are supported by measurements on the stratification of the elements within the particle and by the observation that the concentration of the species found in the outer layer is proportional to the reciprocal of the particle diameter.
2.1 INTRODUCTION

Coal is still the major source of atmospheric particulates, inspite of improvements in combustor operation and the implementation of electrostatic precipitators and scrubbers for particulate emission control. Interest in the control of fine particles emitted by pulverized coal combustion is motivated by environmental considerations since the fine particles can penetrate deep into the lungs, have long atmospheric residence times, and are believed to contain relatively high concentrations of toxic trace species. Studies of the size distribution of the fly ash emitted by utility boilers (Markowski, et. al., 1980; McCain et. al., 1975) show that most of the fly ash is concentrated in a size range of 1 to 20 microns but that a small amount, of the order of one to two percent of the total ash by weight is present in the submicron size range which shows up as a distinct spike in the particle size distribution. Studies of the composition of the larger ash particles have shown that these have concentrations of the volatile trace species that increase with decreasing particle size (Davison et. al., 1974) and that the surface layers of the particles are
enriched in the same trace species (Linton et. al., 1977).

Fly ash is formed from the high temperature physical and chemical transformation of the mineral matter present with the parent coal. The ash forming constituents of coal have been categorized as inherent, adventitious, or extraneous. The inherent mineral matter encompasses those inorganic elements intimately or chemically bonded to the carbonaceous matter of the coal because of their association with the original plant material or as a result of ion-exchange processes with circulating ground water during the coal formation period. Adventitious mineral matter is present as finely distributed micron sized mineral crystallites in the carbonaceous material. Because of the association of adventitious mineral matter with the carbonaceous material, the mineral inclusions can also be categorized as inherent. Extraneous mineral matter is free dirt from adjacent sedimentary bands without any appreciable association with the carbonaceous material. The major, minor, and trace element content in coals are listed in Table 2.1 as an average of 100 US coals. The major constituents, which include; Si, Al, Fe, Ca, and Mg generally occur in common earth minerals, the most abundant being quartz, kaolinite, calcite, and pyrite. With respect to their vaporization and condensation characteristics, the inorganic elements can be categorized as refractory or volatile depending on their volatility and/or abundance in the parent coal. The refrac-
Table 2.1 - Mean composition for 100 coals

<table>
<thead>
<tr>
<th>CONSTITUENTS</th>
<th>MEAN</th>
<th>STANDARD DEVIATION</th>
<th>MIN</th>
<th>MAX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractory</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1.29 %</td>
<td>0.45</td>
<td>0.43</td>
<td>3.04</td>
</tr>
<tr>
<td>Ca</td>
<td>0.77 %</td>
<td>0.55</td>
<td>0.05</td>
<td>2.67</td>
</tr>
<tr>
<td>Fe</td>
<td>1.92 %</td>
<td>0.79</td>
<td>0.34</td>
<td>4.32</td>
</tr>
<tr>
<td>Mg</td>
<td>0.05 %</td>
<td>0.04</td>
<td>0.01</td>
<td>0.25</td>
</tr>
<tr>
<td>Si</td>
<td>2.49 %</td>
<td>0.80</td>
<td>0.58</td>
<td>6.09</td>
</tr>
<tr>
<td>Volatile</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>14.02 PPM</td>
<td>17.7</td>
<td>0.50</td>
<td>93.00</td>
</tr>
<tr>
<td>Cd</td>
<td>2.52 PPM</td>
<td>7.60</td>
<td>0.10</td>
<td>65.00</td>
</tr>
<tr>
<td>Cr</td>
<td>13.75 PPM</td>
<td>7.26</td>
<td>4.00</td>
<td>54.00</td>
</tr>
<tr>
<td>Hg</td>
<td>0.20 PPM</td>
<td>0.20</td>
<td>0.02</td>
<td>1.60</td>
</tr>
<tr>
<td>Ni</td>
<td>21.07 PPM</td>
<td>12.35</td>
<td>3.00</td>
<td>80.00</td>
</tr>
<tr>
<td>Pb</td>
<td>34.78 PPM</td>
<td>43.69</td>
<td>4.00</td>
<td>218.00</td>
</tr>
<tr>
<td>Sb</td>
<td>1.26 PPM</td>
<td>1.32</td>
<td>0.20</td>
<td>8.90</td>
</tr>
<tr>
<td>Zn</td>
<td>27.29 PPM</td>
<td>694.23</td>
<td>6.00</td>
<td>5350.00</td>
</tr>
<tr>
<td>Ultimate Analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>70.28 %</td>
<td>3.87</td>
<td>55.23</td>
<td>80.14</td>
</tr>
<tr>
<td>H</td>
<td>4.95 %</td>
<td>0.31</td>
<td>4.033</td>
<td>5.79</td>
</tr>
<tr>
<td>N</td>
<td>1.30 %</td>
<td>0.22</td>
<td>0.78</td>
<td>5.79</td>
</tr>
<tr>
<td>O</td>
<td>8.68 %</td>
<td>2.44</td>
<td>4.15</td>
<td>16.03</td>
</tr>
<tr>
<td>Ash</td>
<td>11.44 %</td>
<td>2.89</td>
<td>2.20</td>
<td>25.80</td>
</tr>
</tbody>
</table>
tory species encompass the non-volatile major oxides while the volatile species encompass the volatile and trace species some of which are potentially toxic (i.e., carcinogens, mutagens, and heavy metals).

At high combustion temperatures, mineral matter will undergo both physical and chemical transformations. The scenario depicting the mechanisms for fly ash formation during pulverized coal combustion is presented in Figure 2.1. The inherent mineral matter is represented as small inclusions averaging around one to two microns (Padia, 1976). Initially, as the coal particle is heated, volatile hydrocarbons originally present in the coal or formed during pyrolysis are vaporized. A residual char particle is left, which proceeds to burn by heterogeneous oxidation of the external surface. For non-swelling coals, the char surface recedes as combustion proceeds, exposing more and more inclusions on the surface. Because ash has a high surface tension, it does not wet the exposed carbon surface, instead these surface inclusions will coalesce to form spherical ash droplets (Ramsden, 1969). Near the tail end of combustion, the char particle will fracture, each leading to the formation of single coalesced ash particle (Padia, 1976). The mineral matter residue of the burned-out suspended coal particles typically have mass mean diameters of 10 to 20 microns and are commonly referred to as residual fly ash. However, not all the ash is released in this way. During combustion, the char combustion
Figure 2.1 - Schematic diagram of fly ash formation during pulverized coal combustion
temperatures (1700 - 2200 K) are high enough that some of the mineral matter will volatilize. As the combustion products are cooled, the inorganic vapors must condense either heterogeneously on the free surface of residual fly ash particles or by homogeneous nucleation if the inorganic vapors become supersaturated thereby leading to the formation of a new condensed phase of extremely small particles. Upon nucleation, the large number of stable nuclei should rapidly grow by coagulation, eventually leading to the formation of particles with mass mean diameter of 0.1 \textmu m (Flagan, 1979; Desrosier, et. al., 1979). The presence of submicron aerosol was first substantiated in the field study of McCain (1975), where the size distribution of fly ash was found to be bimodal. Results from a more recent study (Marcowski, 1980) are presented in Figure 2.2. It should be noted that particles greater than ten microns which were collected in the preseparator of the cascade impactor have been lumped and subsequently classified as having particle diameters of ten microns. Studies of the composition of the residual fly ash particles have shown that these have concentrations of volatile trace species that increase with decreasing particle size (Davison, et. al., 1974) and that the surface layers of the particles are enriched in the same species (Linton, et. al., 1977). This is consistent with the hypothesis that the trace metal vapors condense on the surface of the residual ash particles produced during pulverized coal combustion with the rate of deposition being controlled by mass transfer.
Figure 2.2 - Fly ash particle size distribution obtained from a utility boiler (Marcowski, 1980)
2.2 OBJECTIVES

In general, the toxic effect of the fine particles (i.e., submicron) are unknown because field data pertaining to their physico-chemical characteristics are fragmentary, and relevant toxicological experiments have not yet been conducted. Furthermore, reevaluation of particulate emission standards will most probably require the reduction in the fine particle emission. In obtaining a better understanding of the evolution of the submicron particles, in situ alteration of the submicron particles through combustion modifications may provide a viable means for reducing both the emission and toxic effect of those particles.

The objectives of this thesis are to determine the physico-chemical characteristics of the submicron particles produced under a wide range of combustion conditions in a laboratory laminar flow furnace and to obtain a better understanding about the evolution of these particles. The analytical capabilities for the specific characterization of the submicron particles will be developed inorder to determine the bulk composition, chemical characteristics of the individual submicron particle (bulk, surface, and depth profile), chemical characteristics of discrete size sampling within the submicron mode, chemical state of inorganic constituents, particle morphology, and particle size distri-
bution (PSD). Since the phenomena of ash vaporization is being examined in detail by Richard Quann (1982), the focus of this thesis will pertain to those processes subsequent to vaporization with specific emphasis on the condensation sequence of the vaporized inorganics, particle growth process by coagulation and agglomeration, and distribution of the vaporized volatile and trace species between the two size modes.
CHAPTER THREE
COMBUSTION AND SAMPLING SYSTEM

The central features of the laboratory scale combustion system are a laminar flow-drop tube furnace, continuous coal feeding system, and water cooled collection probe for continuous recovery and quenching of the combustion products followed by an Andersen impactor for on line size classification of the residual fly ash particles. The advantages of conducting combustion experiments on such an apparatus are that: (1) the combustion conditions can be precisely defined, controlled, and monitored to permit detailed investigation of a number of parameters effecting particle formation; (2) small homogeneous samples of well characterized coal are employed for the experiments; (3) all particulate products leaving the furnace can be completely collected and size classified for subsequent analysis which eliminates questions inevitably present in field studies to the extent that collected samples are representative; and (4) the laboratory system can simulate environments encountered in both conventional pulverized coal fired boilers and extreme conditions such as those proposed for advanced energy conversion systems (e.g., MHD).

In this chapter, the combustion furnace, continuous
coal feeding system, collection system, monitoring capabilities, and operating parameters are described in detail.

3.1 COMBUSTION FURNACE

A schematic diagram of the laminar flow-drop tube furnace (Astro Model 1000a) is presented in Figure 3.1. The furnace has electrically heated graphite elements, the temperature of which are regulated with an automated current controller. In order to protect the graphite heating elements from the oxidizing environment, the elements are isolated from the central combustion zone by an alumina muffle tube. Due to the thermal limitation imposed by the alumina, the maximum operating furnace temperature is 1800 Kelvin. The main gas, a pre-mixed oxygen inert gas, enters at $1.0 \times 10^{-4}$ m$^3$/s through the top of the furnace where it flows through an alumina honeycomb at the top of the hot zone, an isothermal region of 0.1 m (House, 1979). The honeycomb serves as both a flow straightener and preheater, delivering the main gas at the specified furnace temperature with a uniform laminar velocity. The composition of oxygen-nitrogen gas mixture is regulated by dual mass flow controllers. Well size classified coal particles are fed through a narrow water cooled feeder tube and injected axially into the main gas stream just below the honeycomb. The coal particles are rapidly heated and combustion begins. Radial dispersion of the particles is minimized by the stable
Figure 3.1 - Schematic diagram of laminar flow furnace
laminar flow field. Visual observation shows that inside the furnace, which has an internal diameter of $5.0 \times 10^{-2} \text{ m}$, the burning particles remain within $6.2 \times 10^{-3} \text{ m}$ of the axis.

Axial temperature profiles of the gas in the hot zone of the furnace were determined by thermocouple measurements. These measurements were performed under flow conditions (6 liters/min main gas) identical to those used in combustion experiments. Coal was not fed, however, for the gas temperature measurements. The measured axial gas temperature profiles were obtained with the water cooled collection probe set at 0.15 m from the honeycomb flow straightener and without the probe, Figure 3.2. At a furnace wall temperature of 1750 K, the average gas temperature in the hot zone of the furnace is 1700 K without the water cooled probe and 1650 K with the water cooled probe. Following the hot zone the gas temperature was cooled at a rate of 2,000 K/s and 7,000 K/s, respectively.

3.2 FEEDER SYSTEM

Because of the experimental scale, the feeding apparatus was designed to feed small quantities of coal continuously and reproducibly. A schematic diagram of the feeding system is presented in Figure 3.3. The coal particles are entrained in $1.0 \times 10^{-6} \text{ m}^3/\text{s}$ of inert carrier gas which flows over the surface of the agitated coal bed and into the stationary fine gauge tubing. The gas velocity in
Figure 3.2 - Gas temperature profiles in laminar flow furnace
Figure 3.3 - Schematic diagram of coal feeder
the fine gauge tubing is sufficient to keep the particles in suspension. The rate of entrainment is established by the rate at which the coal feed vial is driven towards the stationary fine gauge tubing by the syringe pump. A range of feeding rates from $1.7 \times 10^{-4}$ grams/s to $1.7 \times 10^{-3}$ grams/s is obtainable by changing the speed of the syringe pump. For a given syringe setting, a fixed clearance between the top of the coal bed and the fine gauge tube will be established after an initial transient. One to three grams of coal are normally fed per experiment.

3.3 COLLECTION PROBE

All the combustion products, both gaseous and solid, are collected at a given height in the furnace by a water cooled probe which is inserted through the bottom of the furnace. The probe position is adjustable to enable time resolved studies. A schematic diagram of the collection probe is presented in Figure 3.4. The inner core of the water cooled collection probe is fitted with a stainless steel porous tubing through which gas is transpired. The $1.27 \times 10^{-2}$ m ID porous tubing is constructed from fused five micron stainless steel spheres. In the top $2.5 \times 10^{-2}$ m section of the probe, the combustion products are rapidly quenched at a rate of $1.0 \times 10^{-4}$ degrees per second by $3.0 \times 10^{-4}$ m$^3$/s of nitrogen. A minimal inward radial gas flow of $6.6 \times 10^{-5}$ m$^3$/s of nitrogen which corresponds to a gas velocity of $3.5 \times 10^{-3}$ m/s is maintained through the subse-
Figure 3.4 - Schematic diagram of water cooled collection probe
quent section of the porous tubing to counter the thermo-
phoretic velocity of the particles (e.g., $1.8 \times 10^{-4}$ m/s),
thereby, preventing particle deposition on the inner wall of
the probe.

3.4 CASCADE IMPACTOR

From the collection probe, the particles and gas
enter directly into an Andersen 20-800 Ambient Sampler for
aerodynamic classification of the particulates. The Andersen
Ambient Sampler is a multistage cascade impactor which
contains eight stages followed by a 0.2 um Fluoropore filter.
Each stage of the impactor contains multicircular jets,
designed to permit highly efficient size classification. The
principle involved in this technique is illustrated in Figure
3.5. The aerosol flow through an orifice (i.e., jet) at a
velocity determined by the size of the orifice. The gas
stream is deflected by a collection plate. Smaller particles
are able to modify their direction of flow and follow the gas
streamlines, while the larger particles possessing a large
kinetic energy impact on the plate. Since the orifice diame-
ter decreases with succeeding stages, the size of impacting
particles will decrease with succeeding stages. The optimal
gas flow rate for this impactor is $4.72 \times 10^{-4}$ m$^3$/s which
will accomodate the high gas flow rates neccessary for
quenching the combustion products.

Several laboratory and field studies (Ondov, 1975;
Figure 3.5 - Schematic diagram showing two stages of a cascade impactor (Friedlander, 1977)
McCain, 1978; and Rao, 1978) have noted that the performance of impactors can be severely hampered by wall loss, reentrainment, and particle bounce. The problems associated with reentrainment and particle bounce can be eliminated by implementing the use of greased aluminum substrate (i.e., apezon grease type H) and minimizing the sampling time to avoid particle overloading on each stage. By incorporating these modifications, the Andersen impactor was recalibrated for the fly ash particles generated in the laboratory furnace. The particle size distribution for each stage was obtained from scanning electron micrographs by an automated image analyser, where between two hundred and five hundred particles were sized. The particle sizing technique will be described in greater detail in section 4.1.2. For each stage the volume mean diameter and the standard deviation for the particle size distribution are presented in Table 3.1. The theoretical volume mean diameter for each stage were calculated for spherical particles with specific density of three (Friedlander, 1977). Due to the close agreement with theory and the observed narrow distribution on each stage, it is evident that problems associated with particle bounce and reentrainment have been eliminated. Significant wall loss has been observed to occur on the inner wall of the inlet nozzle. Consequently, the inlet nozzle was redesigned so that gases could be transpired through its inner porous graphite wall to eliminate particle deposition. The recovery of selected inorganic elements on the impactor stages and
Table 3.1 - Calibration of the ambient Andersen impactor

<table>
<thead>
<tr>
<th>stage number</th>
<th>experimental</th>
<th></th>
<th>Theory*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$D_p$</td>
<td>$r$</td>
<td>$D_p$</td>
</tr>
<tr>
<td>0</td>
<td>12.2</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>5.65</td>
<td>1.8</td>
<td>5.52</td>
</tr>
<tr>
<td>2</td>
<td>3.46</td>
<td>0.46</td>
<td>2.47</td>
</tr>
<tr>
<td>3</td>
<td>2.54</td>
<td>0.37</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>1.58</td>
<td>0.20</td>
<td>0.95</td>
</tr>
<tr>
<td>5</td>
<td>0.9</td>
<td>0.23</td>
<td>0.54</td>
</tr>
<tr>
<td>6</td>
<td>0.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* particle density= 3.0 g/cc
final filter should verify whether significant wall loss of inorganic particles is occurring. The percentage of selected elements in the coal feed ultimately recovered after combustion are presented in Table 3.2. Generally, more than ninety percent of an element in the coal feed is recovered in the particulate product. This indicates that no significant loss of particles or inorganic vapors are occurring within the furnace, collection probe, or Andersen Impactor.

The submicron particulates, because of their small size pass through the impactor. Three sampling methods presently employed for the preparation of the submicron particles for the various analytical techniques are; (1) collection on a filter for subsequent weight and chemical analysis; (2) deposited on transmission electron microscope grids in the electrostatic precipitator for microscopy studies; and (3) on-line size classification by mobility classifier. These various option will be descused in greater detail in chapter four.
Table 3.2 - Elemental material balance on furnace and collection system. Gas temperature 1750 K, oxygen partial pressure 0.5 atmospheres

<table>
<thead>
<tr>
<th>Element</th>
<th>percent recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>77.3</td>
</tr>
<tr>
<td>As</td>
<td>99.6</td>
</tr>
<tr>
<td>Ca</td>
<td>96.0</td>
</tr>
<tr>
<td>Cr</td>
<td>100.5</td>
</tr>
<tr>
<td>Fe</td>
<td>91.7</td>
</tr>
<tr>
<td>La</td>
<td>100.4</td>
</tr>
<tr>
<td>Mg</td>
<td>80.7</td>
</tr>
<tr>
<td>Mn</td>
<td>90.0</td>
</tr>
<tr>
<td>Na</td>
<td>89.0</td>
</tr>
<tr>
<td>Sb</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Insight on the fundamental processes governing the nature of the submicron particles can be obtained from a detailed physicochemical characterization of the submicron particles. A list of the analytical techniques used in this study are presented in Table 4.1. The focus of this section will be to evaluate the analytical capability of each technique for quantitative analysis.

4.1 TRANSMISSION ELECTRON MICROSCOPE

A Philips 200 transmission electron microscope (TEM), with a working magnification of 125,000 x, was used for morphological characterization of the submicron particles. The high resolution of the TEM is obtained with a highly collimated electron beam, where a point to point resolution of several angstroms can be achieved. The electrons are produced by thermionic emission from a heated tungsten "hairpin" filament held at -100 kV. The emitted electrons are accelerated and partially collimated by a controlling wehnelt electrode surrounding the filament. With magnetic lenses, the electron beam is first condensed and then focused onto the electron thin specimen held in the specimen stage.
Table 4.1 - Analytical instrumentation used for physico-chemical characterization of the submicron particles

<table>
<thead>
<tr>
<th>INSTRUMENT</th>
<th>APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical Characterization</strong></td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td>particle morphology</td>
</tr>
<tr>
<td>Automated image analyzer</td>
<td>PSD</td>
</tr>
<tr>
<td>Mobility classifier</td>
<td>discrete sized Samples within the submicron mode</td>
</tr>
<tr>
<td><strong>Chemical Characterization</strong></td>
<td></td>
</tr>
<tr>
<td>INAA, AA, and liquid chromatography</td>
<td>bulk analysis</td>
</tr>
<tr>
<td>STEM</td>
<td>individual particle analysis</td>
</tr>
<tr>
<td>Auger spectroscopy</td>
<td>surface analysis</td>
</tr>
<tr>
<td>ESCA, mssbauer, and x-ray diffraction</td>
<td>chemical state</td>
</tr>
</tbody>
</table>
The transmitted electrons are then magnified to form a planar image of the specimen on the viewing screen at the bottom of the microscope column. Micrographs of the images are obtained with a plate camera which is located below the viewing screen.

Samples of the submicron particles are prepared by depositing the particles on transmission electron microscope grid placed in an electrostatic precipitator down stream of the cascade impactor. The TEM grid is a 200 mesh copper grid with a vacuum deposited carbon support film. By allowing the electrostatic precipitator to fill uniformly with particles before each pulse of the collection plate electrode, representative samples of the submicron particles can be obtained.

Quantitative calibration of the magnification settings for the Philips 200 was obtained with a carbon diffraction grading replica standard, containing 2,160 diffraction lines per millimeter. At low magnification the distance between the large number of lines is used, while at high magnification the distance between two discrete points is used. The calibration of the magnification setting are compared with the manufacture's for the Philips 200, Table 4.2. Due to slight drift in the magnification settings with time, recalibrations were periodically conducted.
Table 4.2 - Calibration of the magnification settings for the Philips 200 TEM

<table>
<thead>
<tr>
<th>magnification setting</th>
<th>manufacture</th>
<th>calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>9,900</td>
<td>8,700</td>
</tr>
<tr>
<td>15</td>
<td>17,000</td>
<td>18,100</td>
</tr>
<tr>
<td>17</td>
<td>30,500</td>
<td>32,100</td>
</tr>
<tr>
<td>19</td>
<td>55,000</td>
<td>58,200</td>
</tr>
<tr>
<td>21</td>
<td>94,000</td>
<td>97,100</td>
</tr>
</tbody>
</table>
4.2 AUTOMATED IMAGE ANALYZER

The particle size distribution of primary particles and agglomerated particles are obtained from TEM micrographs of the submicron particles by an automated image analyzer (Magiscan). The automated image analyzer is a computerized system with the software capabilities for establishing equivalent spherical diameter of both primary and agglomerated particles. Since the growth process by coagulation is instantaneously frozen upon sampling with the collection probe, time resolved studies can be used to examine coagulation kinetics where the relative rate of coalescence leads to the formation of either single spherical particles or agglomerated particles.

4.3 MOBILITY CLASSIFIER

The mobility classifier (Knutson and Whitby, 1975) is an on line instrument developed for particle size classification of submicron particles where the classification is based on the electrical mobility of unicharged particles. An added feature of the mobility classifier is its capability for extracting discrete sized samples.

In order to obtain discrete sized samples of the primary particles for bulk chemical analysis, the mobility classifier had to be calibrated with respect to the inorganic submicron particles since slight agglomeration of these particles will occur before sampling. The primary particle
size distributions for the discrete sized cuts obtained from the mobility classifier are broader than that predicted from theory. However, the breadth of the particle size distributions, which is a consequence of agglomeration, will not pose a significant problem in obtaining several discrete sized cuts of the primary particles within the submicron particle mode. The calibration was conducted for submicron particles produced from the combustion of Montana Lignite (53/63 um) at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen. The new voltage settings verse mean diameters for the primary particles are presented in Figure 4.1.

4.4 Bulk Analysis

The bulk elemental composition for the major, minor, and trace inorganic elements is determined by instrumental neutron activation analysis (INAA) supplemented with atomic absorption (AA) for silicon, potassium, and phosphorus, and liquid chromatography (Mizisir et. al., 1978) for sulfur. INAA, a multielemental analysis technique, is a reliable and sensitive method for the determination of trace elements in amounts of one nanogram or less. The technique employs a high neutron flux source for the production of radionuclides (i.e., isotopes) from the target element. The radionuclides decay, leading to the emission of gamma rays of specific energy which are measured with a gamma spectrometer, a Ge(Li)
Figure 4.1 - Calibration of the mobility classifier with respect to primary particle diameter
A solid state detector coupled to a multichannel analyzer. The precise and accurate amount of each element in the sample is calculated by ratioing the measured activity of the sample with the activity of a standard of known composition (i.e., NBS coal). The accuracy of INAA was checked by analyzing several Opal Glass samples "NBS standard number 91". The composition of the oxides of Ca, Al, and Na as determined by INAA are within one percent of the NBS composition, Table 4.3.

The submicron particles are collected on 0.2 micron high purity filter (i.e., Fluoropore) placed in the filter stage of the cascade impactor. The fluoropore filters are a polytetrafluoroethylene substrate bonded to high density polyethylene net for improved ease of handling.

4.5 SCANNING TRANSMISSION ELECTRON MICROSCOPE

The elemental composition of individual primary particles are obtained with a 100kv field emmission scanning transmission electron microscope (STEM) fitted with an energy dispersive x-ray spectrometer. In order to obtain accurate, quantitative results a computerized data acquisition system, known as quantex-ray, is available for x-ray evaluation. The STEM provides a wide range of image and analysis capabilities not previously combined in a single instrument, representing a major advance in instrumental microanalysis (Vander Sande and Hall, 1979). The unique feature of the STEM is its
Table 4.3 - INAA analysis of Opal Glass, NBS standard number 91

<table>
<thead>
<tr>
<th>element</th>
<th>INAA</th>
<th>NBS analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>34.5%</td>
<td>34.1%</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>24.8%</td>
<td>24.1%</td>
</tr>
<tr>
<td>CaO</td>
<td>40.7%</td>
<td>41.8%</td>
</tr>
</tbody>
</table>
spatial resolution of twenty angstroms for elemental analysis. This permits microprobe analysis of the individual primary particles where the contribution from adjacent particles can be neglected.

Submicron particle samples for the STEM are prepared by depositing the submicron particles on transmission electron microscope grid placed in the electrostatic precipitator down stream of the cascade impactor.

When X-ray spectra of standards and samples in the STEM are acquired, there exists some uncertainty in the analysis, culminating from both systematic and random errors. The approach taken in minimizing the systematic errors are outlined in Table 4.4.

4.5.1 Reproducability

A. Beam Current Decay

The decay in beam current results from contamination build up on the filament of the field emission gun, the rate of which depends on the gun chamber vacuum (Garret-Ried, 1979). The significance of beam current decay arises from the fact that the intensity of induced x-ray emission from the specimen is directly proportional to beam current (Goldstien and Williams, 1977). After cleaning the filament with a high current pulse, the objective aperture current (indirect monitor of beam current) and count rate for inconel
Table 4.4 - Sources of error and corrections implemented in order to obtain quantitative x-ray analysis of the submicron particles with the STEM

<table>
<thead>
<tr>
<th>Phenomena</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Reproducibility</td>
<td></td>
</tr>
<tr>
<td>A. Decaying probe current</td>
<td>monitor for each analysis</td>
</tr>
<tr>
<td>B. Specimen contamination</td>
<td>bake samples before analysis</td>
</tr>
<tr>
<td>C. Drift</td>
<td>mechanically realign sample</td>
</tr>
<tr>
<td>D. Counting statistics</td>
<td>determine the uncertainty in x-ray counting and propagate through calculation</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>II. Maximize signal/bremsstrahlung</td>
<td></td>
</tr>
<tr>
<td>A. Bremsstrahlung</td>
<td>establish spurious sources and eliminate contribution</td>
</tr>
<tr>
<td>B. Hole count</td>
<td>use virtual objective aperture in back focal plane</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>III. Quantitative analysis</td>
<td></td>
</tr>
<tr>
<td>A. Thin film criteria</td>
<td></td>
</tr>
<tr>
<td>1. Absorption</td>
<td>establish significance of absorption, fluorescence, and beam spreading making the necessary adjustment to raw intensities</td>
</tr>
<tr>
<td>2. Fluorescence</td>
<td></td>
</tr>
<tr>
<td>3. Beam spreading</td>
<td></td>
</tr>
<tr>
<td>B. Standards</td>
<td>implement use of experimental sensitivity factors $K_{ab}$</td>
</tr>
<tr>
<td>C. Specimen stability</td>
<td>establish stable species</td>
</tr>
</tbody>
</table>
600 standard (i.e., Iron) were monitored for 1500 seconds, Figure 4.2 (Was, 1980). X-ray analysis obtained at different time intervals during the decay cycle will hamper comparative analysis of the raw intensity.

The variation in x-ray intensities resulting from decaying beam current could be eliminated by decreasing the acquisition time and cleaning the filament before each analysis. However, this would sharply decrease the life of the filament and subsequently increase instrument down time. Instead, the corrective procedure used was to normalize the x-ray intensities with respect to beam current.

B. Specimen Contamination

Contamination build up on the specimen surface will attenuate both the primary electrons and x-ray signal of the specimen. The effect of contamination build up during analysis is illustrated in Figure 4.2, where the count rate for Fe drops off more sharply than the objective aperture current with time. The effect of contamination build up is more serious for the light elements (e.g., Na and Mg), since their low energy x-rays will be attenuated more severely.

During analysis, surface adsorbed hydrocarbon and carbon oxides (i.e., contamination) will coke under the high energy electron beam leaving a residual film of carbon (Ennos 1953; Heide, 1963). In the high vacuum sample chamber, the rate of residual vapor deposition will be extremely slow.
Figure 4.2- Decay in beam current and specimen count rate with time
Therefore, the observed contamination build up during analysis has been attributed to the migration of surface adsorbed hydrocarbons and carbon oxides into the analysis region. Proper sample preparation by removing adsorbed contaminates will eliminate substantial contamination build up during analysis. This is achieved by baking the TEM grids at 200 centigrade in a vacuum of $10^{-6}$ torr for an hour.

C. Drift

For extended counting periods (i.e., >20 seconds), the drift of the specimen can occur such that the particle of interest is no longer being analyzed. Specimen drift results from expansion of the carbon support film with heating, and/or movement in the specimen holder or retaining ring due to vibrations. In order to compensate for drift during analysis, continual realignment of the specimen will be required.

D. Counting Statistics

Since x-ray photon emission is a random process, some variance (i.e., counting error) in the measured intensities will exist for a series of repetitive analyses. For a measurement of acquired counts, $N$, the standard counting error is represented by the relationship (Kevex, 1980)

$$
\sigma = (N)^{1/2}
$$

Eq. 4.1
For a series of repetitive analyses of a submicron particle, the standard deviation in the normalized counts for Si and Fe was determined and is compared with the standard counting deviation in Table 4.5. The close agreement indicates that the contribution from all sources of error other than counting error are relatively small.

The precision of each analysis which is defined by the relationship

\[ \text{Precision} = \frac{\sigma}{N} = \frac{1}{(N)}^{1/2} \quad \text{Eq. 4.2} \]

can be greatly enhanced by increasing the acquisition time (i.e., number of counts) while maintaining a high signal to background ratio.

4.5.2 Maximize Signal/Bremstrahlung

A. Bremsstrahlung

Background is the result of the detection of unwanted x-rays or electrons. The primary source of background originates from inelastic collision of the primary electrons with the specimen, resulting in the production of a continuum of x-rays. This continuum is sometimes referred to as bremsstrahlung or braking radiation. The high background level detracts from the statistical precision of the results by increasing the difficulty in interpreting the signal from
Table 4.5 - Repetitive analysis of submicron particles for the elements silicon and iron.

<table>
<thead>
<tr>
<th>number</th>
<th>total count</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>258</td>
<td>187</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>269</td>
<td>226</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>311</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>268</td>
<td>199</td>
<td></td>
</tr>
<tr>
<td></td>
<td>276</td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>average</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>standard deviation</td>
<td>23</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>standard counting deviation</td>
<td>17</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>
Because of the low counting rates and high background, minimization of the extraneous bremsstrahlung, the source of which can be traced by the presence of spurious x-rays, will be essential for data reduction. From examination, the largest source of bremsstrahlung was attributed to the copper grid matrix whose x-ray signal dwarfs the specimen signal, Figure 4.3 (a). The explanation for the unusually high production of spurious x-rays (i.e., grid matrix) was resolved by examining the hole count. Here, the electron beam is directed through a hole in a specially prepared thin foil standard. For a perfectly convergent beam, no interactions between the electron beam and standard should occur. However, extremely high hole counts were detected (Was, 1980). The close proximity of the objective aperture to the specimen causes the scattering of the electron beam which accounts for the high hole count. The high hole count was eliminated by shifting the objective aperture into the back focal plane. Consequently, a sharp reduction in the spurious x-ray and bremsstrahlung emanating from the copper grid matrix was achieved. This is illustrated in Figure 4.3 by examining the x-ray spectra before (a) and after (b) modifying the objective aperture configuration. The increase in x-ray counts from the specimen is a direct result of the increased current density due to improved convergence of the electron beam.
Figure 4.3 - STEM x-ray spectra before (A) and after (B) modifying the aperture configuration.
4.5.3 Quantitative Analysis

A. Thin Film Criterion

The thin film criterion states that no adsorption or fluorescence corrections need be applied if the specimen is infinitely thin. Many people interpret this criterion to mean that if the film is transparent to electrons (i.e., electron thin) at the operating potential being employed, the thin film criterion is satisfied. However, absorption effects can be appreciable for electron thin films (Tixier, 1979), if the combination of mass absorption coefficient and film thickness are large enough. For this reason, the theoretical extent of absorption and fluorescence were examined for a range of film thicknesses.

The extent of absorption can be calculated to first approximation, if one considers that the average depth of x-ray excitation occurs at one half the thickness of the film. If the path length for absorption in the film is represented as \((tc\csc{\alpha})/2\), the generalized form of the equation reduces to

\[
K_{ab} = K_{ab}^{\text{T.F.}} e^{-\left(\frac{\Delta X_{b-a}}{\rho \text{spec}}\right) \left(\frac{\rho t}{2}\right)} \quad \text{Eq. 4.3}
\]

\[
\Delta X_{b-a} = \frac{u}{\rho_b} - \frac{u}{\rho_a} \csc \alpha
\]
where $K_{ab,T.F.}$ is the $K_{ab}$ ratio for an infinitely thin film, \( u/\rho_{b}^{spec} \) and \( u/\rho_{a}^{spec} \) are mass absorption coefficient for characteristic x-rays of element $a$ and $b$ in the thin film (spec), respectively, $\alpha$ is the take off angle, and $t$ is the electron path length (Goldstien et. al., 1977). The magnitude of the binary absorption coefficient will increase as the difference between the atomic number of the two elements increases. The calculated absorption factors for Mg and Al relative to Fe are presented in Figure 4.4, where the absorption coefficients were obtained from the literature (Bender et. al., 1980; Henke et. al., 1956). The effect of x-ray absorption can be neglected for particles less than 750 angstroms in diameter.

The extent of fluorescence is calculated from the relationship

\[
\frac{I_{f}^{a}}{I_{a}} = 2 W_{b} C_{b} \frac{r_{a}}{r_{a} - 1} \frac{A_{a}}{A_{b}} \frac{u}{\rho_{a}} \frac{u}{\rho_{b}^{spec}} \frac{E_{ca}}{E_{cb}} (\rho t)^{2} \quad \text{Eq. 4.4}
\]

where $I_{f}^{a}$ is the fluorescence intensity which is added to the primary intensity $I_{a}$, $W_{b}$ is the fluorescence yield for element $b$, $r_{a}$ is the absorption jump ratio for element $a$, \( u/\rho_{a} \) is the mass absorption coefficient of element $b$'s radiation in element $a$, $A_{a}$ and $A_{b}$ are the atomic weights of element $a$ and $b$, and $E_{ca}$ and $E_{cb}$ are the critical excitation energies for the characteristic lines of elements $a$ and $b$. 
Figure 4.4 - Adsorption correction for various particle diameters
(Philibert et al., 1975). From equation 4.4, the fluorescence of the detected elements in the submicron particles were calculated to be less than one percent for particles less than 1000 angstroms in diameter.

The spatial resolution for analysis is assumed to be on the order of twenty angstroms (i.e., beam diameter). However, electrons are elastically scattered as they pass through the specimen. Consequently, the analysis volume from which x-rays are produced can exceed the primary electron beam diameter depending on the extent of beam spreading. Goldstien et al. (1977) has estimated the effective electron beam spreading or broadening,

\[
b = 625 \frac{Z}{E_o} \frac{\rho}{A} \frac{1}{2} t \frac{3}{2}
\]

Eq. 4.5

where \( b \) is the extent of broadening for a zero diameter beam, \( Z \) is the atomic number, \( A \) is the atomic weight, \( E_o \) is the accelerating voltage in KeV, \( \rho \) is the density of the film, and \( t \) is specimen thickness. Calculated values of beam broadening for a zero diameter beam as a function of film thicknesses for pure element targets are presented in Figure 4.5. In summary beam broadening will be appreciable for particles greater than 250 angstroms in diameter. Consequently, the effect of beam broadening will have to be considered before comparing the raw intensities from various sized particles.
Figure 4.5 - Beam broadening for various particle diameters.
B. Standards

Quantitative x-ray microanalysis of a submicron particle is simplified, since the effect of adsorption and fluorescence can be ignored. A simple ratio technique known as the Cliff and Lorimer method was used to obtain direct quantitative analysis in weight percent. For binary mixtures, the weight percent is determined from the x-ray intensities by the relationship,

\[ \frac{C_a}{C_b} = K_{ab} \frac{I_a}{I_b} \]  

Eq. 4.6

where \( I \) is the measured x-ray intensity, \( C \) is the weight fraction of the species, and \( K \) is the sensitivity correction factor. The factor, \( K \), accounts for the relative efficiency of x-ray production by the analyzed element and the detection efficiency of the x-rays at their characteristic energies.

Analysis of multicomponent mixtures can be achieved by developing a series of \( K \) factors from binary mixtures and referencing all \( K \) factors to the response of one element. The weight fraction of species \( i \) can be determined by dividing the adjusted intensity for species \( i \) by the sum of the adjusted intensity of all species detected.

\[ C_i = \frac{K_i I_i}{\sum K_j I_j} \]  

Eq. 4.7

Where \( \sum C_i = 1 \)
The sensitivity correction factors for quantitative x-ray analysis are determined from bulk standards, thin foil standards, or calculated from theory (Goldstien, 1979). For the application of thin film analysis, the sensitivity correction factors determined from bulk standards will have to be adjusted to account for the effects of x-ray adsorption and fluorescence (i.e., ZAF corrections). The procedure for ZAF corrections has been outlined in the previous section. Since thin foil standards, which are of known mass thickness, meet the thin foil criterion, ZAF corrections are not needed. Sensitivity correction factors can also be directly calculated from theory by establishing for each element: the ionization cross section, the fluorescence yield, the fraction of total intensity measured, and the adsorption characteristics of the EDS detector. Because of the uncertainty in the absorption characteristics of the EDS detector due to nonuniformity in manufacturing of the beryllium window (Kevex, 1980), the theoretically calculated sensitivity correction factors may not properly estimate the extent of absorption of the low energy x-rays (i.e., light elements) by the detector window. This is evident from the comparison of experimentally determined sensitivity correction factors (Cliff and Lorimer, 1975) with theoretically calculated sensitivity correction factors (Goldstien, 1977). The underestimation of the K factors for the light elements by Goldstien (i.e., Na and Mg) arises due to uncertainty in the
The approach used in establishing the sensitivity correction factors for the STEM was derived from the combination of the three techniques. Because of the uncertainty in adsorption characteristics of the detector (i.e., window thickness), sensitivity correction factors for the light elements had to be determined experimentally. From a Mg-Fe thin film standard, the sensitivity correction factor for Mg relative to Fe was found to be 7.5 (Hall, 1978). From a Mg-Si bulk standard, the sensitivity correction factor for Mg relative to Si after ZAF corrections was found to be 6.7. For the remaining elements of interest, the sensitivity correction factors were calculated from theory. The derived sensitivity correction factors which have been referenced to sulfur are presented in Figure 4.6. The unusually high K values for the light elements (i.e., Mg and Si) results from the high adsorption of their low energy x-rays by the thin mylar film which has been placed on the outer surface of the beryllium window in order to absorb the low energy electrons.

By comparing the average concentration for the primary particles determined from the STEM with the bulk composition of submicron particles by INAA, the use of the derived sensitivity correction factors for quantitative analysis of the submicron particles can be justified, Table 4.7. The variation in the relative concentration of Mg, Si, Ca, and Fe by the STEM with that by INAA can be attributed to
Table 4.6 - Theoretical and experimentally determined sensitivity correction factors $K_{x/Si}$ for 100 kV.

<table>
<thead>
<tr>
<th>Z</th>
<th>$K_{\text{experimental}}$ (Cliff, 75)</th>
<th>$K_{\text{theoretical}}$ (Goldstien, 77)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Na</td>
<td>5.77</td>
<td>1.66</td>
</tr>
<tr>
<td>12 Mg</td>
<td>2.07</td>
<td>1.25</td>
</tr>
<tr>
<td>13 Al</td>
<td>1.47</td>
<td>1.12</td>
</tr>
<tr>
<td>14 Si</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>20 Ca</td>
<td>1.00</td>
<td>1.02</td>
</tr>
<tr>
<td>26 Fe</td>
<td>1.27</td>
<td>1.33</td>
</tr>
</tbody>
</table>
Figure 4.6 - STEM Sensitivity correction factors referenced to sulfur
<table>
<thead>
<tr>
<th>element</th>
<th>conc. (wt%)</th>
<th>conc. (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STEM</td>
<td>INAA</td>
</tr>
<tr>
<td>Mg</td>
<td>64.4 + 6.1</td>
<td>60.3</td>
</tr>
<tr>
<td>Si</td>
<td>4.1 + 0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>P</td>
<td>1.2 + 0.2</td>
<td>3.3</td>
</tr>
<tr>
<td>S</td>
<td>0.7 + 0.1</td>
<td>5.4</td>
</tr>
<tr>
<td>K</td>
<td>0.5 + 0.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Ca</td>
<td>13.3 + 1.3</td>
<td>11.9</td>
</tr>
<tr>
<td>Fe</td>
<td>+</td>
<td>14.1</td>
</tr>
</tbody>
</table>
the inherent counting error for STEM analysis. However, the apparent breakdown in analysis for S, K, and P can only be explained by examining the stability of those elements under the high intensity electron beam. This will be discussed in greater detail in the following section.

C. Sample Stability

Morphological changes in the internal structure of the particle under the high intensity electron beam was observed. The observed mobility within the particle may be explained in terms of localized heating on an atomic level. The stability of each element was examined in order to determined whether preferential loss of some of the elements was occurring during analysis. In comparing the average concentration of the primary particle with the bulk composition of the submicron particles by INAA, Table 4.7, the volatile species S, P, and K were found to be substantially depleted. The loss phosphorous has been noted in the analysis of biological specimen (Sudenfield, 1979). The stability of the elements Si, Ca, Fe, Mg, and S were examined in more detail where the total counts after each of four consecutive analyses were compiled. The results are presented in Table 4.8. The behavior of the volatile species, as represented by S, clearly demonstrates their instability under the high intensity electron beam. The variation in the total counts for Si, Mg, and Fe are attributed to the inherent counting error for x-ray analysis. The gradual decrease in Ca with
<table>
<thead>
<tr>
<th>Element</th>
<th>Intensities*</th>
<th>Standard Counting Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(time sec)</td>
<td>150</td>
</tr>
<tr>
<td>Mg</td>
<td>494</td>
<td>485</td>
</tr>
<tr>
<td>Si</td>
<td>187</td>
<td>226</td>
</tr>
<tr>
<td>Ca</td>
<td>512</td>
<td>531</td>
</tr>
<tr>
<td>Fe</td>
<td>258</td>
<td>269</td>
</tr>
<tr>
<td>S</td>
<td>93</td>
<td>72</td>
</tr>
</tbody>
</table>

* Normalized to beam current
successive analysis can not be justified by the counting error alone, however, Ca will be incorporated into the analysis, since its retention for the first 200 seconds is bounded within the uncertainty for x-ray analysis.

Quantitative x-ray microanalysis will only be conducted for the elements Si, Ca, Fe, and Mg where the error in analysis will be specified by the counting error.

4.6 AUGER SPECTROSCOPY

The surface sensitive technique of Auger Spectroscopy (Powell and Spicer, 1978; Kane and Larraby, 1974) was used to extract information about the elemental stratification within the submicron particle. The system used was a Physical Electronic 590A Scanning Auger Microprobe with submicron spatial resolution of 0.2 um for analysis. The 590A utilizes both single pass electron optics for image analysis, and an Ar ion sputtering gun for depth profiling. Auger Spectroscopy is a highly surface sensitive technique. Since the number of escaping Auger electrons from the sample decays exponentially with distance into the sample matrix, the analysis should represent the composition of the first few atomic layers. Because the Auger peaks are superimposed on a continuous background from the secondary electron emission, the Auger signal is more readily detected by differentiating the energy distribution function (e.g., $dN(E)/dE$). The submicron particles are collected on a silver membrane filter
(0.2 um pore size) which eliminates severe sample charging during analysis.

The Auger electron yield with primary beam energy, $E_p$, is largely determined by the electron impact ionization cross section of the core level involved in the Auger transition. The optimum Auger yield for the range of elements present in the fume will be obtained for a primary beam energy of 5 KeV. The other important instrumental parameters for peak enhancement are the primary electron current ($I_p$), the sensitivity (sens), and, for the conventional $dN(E)/dE$ spectrum, the modulation energy ($E_m$). In order to ensure quantitative analysis, the response of the peak to peak amplitude with instrumental parameters need to be examined for both the low and high energy Auger signals.

The Auger peak to peak amplitude increases linearly with beam current as shown for Mg LMM Auger signal (32 eV) and Mg KLL Auger signal (1174 eV) in Figure 4.7. However, for excessively high beam current densities and accelerating voltages, this linear relationship will break down due to beam damage of the specimen. Consequently, during analysis the beam current will be maintained below one microamp for accelerating voltage of 3 and 5 kV. Under these operating conditions no significant loss of the volatile species is evident. The very slight decay in the signal from homogeneous standards with time is attributed to contamination build up on the specimen surface, since the signal returns to its
Figure 4.7 - Auger peak amplitude verse beam current
original amplitude upon cleaning with the ion gun.

For S LMM Auger signal (152 eV), the peak to peak amplitude increases linearly over the entire range of sensitivity settings, Figure 4.8.

The Auger peak to peak amplitude for Mg LMM Auger signal (32 eV) and S KLL Auger signal (2117 eV) verses modulation energy is shown in Figure 4.9. The Auger peak to peak amplitude is proportional to the modulation energy when the modulation energy is small relative to the Auger peak width. However, as the modulation energy is increased, the Auger peak width is instrumentally broadened. Consequently, the peak to peak amplitude will becomes nonlinear as the modulation energy is increased. The peak to peak amplitude of Mg LMM Auger signal (32 eV), with its correspondingly narrow peak width, becomes nonlinear for modulation energy greater than 2 eV. Since the peak width increases with electron energy, the peak to peak amplitude of the S KLL Auger signal (2114 eV) increase linearly through a modulation energy of 8 eV. Therefore, in using modulation energy to enhance the peak to peak amplitude, the extent of nonlinearity for the various elements must be incorporated into the peak to peak normalization.

Theoretically, quantitative analysis of the mass concentration for the surface layers can be determined from the peak to peak amplitudes with the use of relative sensi-
Figure 4.8 - Auger peak amplitude verse sensitivity setting
Figure 4.9 - Auger peak amplitude verse modulation amplitude setting.
tivity factors. The effects of surface topography (e.g., roughness) is believed to decrease all Auger signals by nearly the same percentage (Fadley, 1974). However, until the full effects of surface roughness are better understood the analysis will only be semi-quantitative. The relative sensitivity factors accommodate for variations in ionization cross sections and escape depths of various Auger electrons for homogeneous samples. The method of generating relative sensitivity factors from homogeneous standards is to normalize the intensities (i.e., peak to peak amplitude) of each element to one specific element (i.e., silver) using the relationship

$$S_{x/Ag} = \frac{a + b}{a} \frac{I_x}{I_{Ag}}$$

where $I_x$ and $I_{Ag}$ are the peak to peak amplitude for element $x$ and pure silver standard, respectively (Davis et. al., 1976). A and b are the chemical formula indices of compound $X_aY_b$. The determination of relative sensitivity factors for quantitative Auger spectroscopy will be highly dependent on the standards chosen. The relative sensitivity factors obtain from standards with small amounts of impurities can lead to substantially errors. Whether the impurity is inherent in the standard, thereby reducing the atomic density, or adsorbed on the surface of the standard (i.e., contamination), thereby leading to the preferential adsorption of the low energy Auger electrons, the relative sensitivity factors will
be inaccurate. The Auger spectra varies dramatically between the metal and the oxide. In the case of magnesium, the peak location and shape (i.e., number of satellite peaks) of the Auger signal varies between the metal and the oxide, but more importantly, the peak to peak amplitude of the differential signal (i.e., dN(E)/dE) appears to be sensitive to the oxidation state of magnesium, Figure 4.10. The Auger spectra for Mg and MgO (Davis et al, 1976) were obtained for a primary beam energy, $E_p$, of 3 KeV. For Mg KLL Auger peak, the sensitivity factor for the oxide (1174 ev) is over three times greater than that for the metal (1186 ev). In addition, the ratio of the relative sensitivity factors of the Mg KLL auger peak to the Mg LMM auger peak is 0.23 for the metal and 1.09 for the oxide. The sensitivity factors for the specific chemical state of the detectable elements in the fume are presented in Table 4.9 for a primary beam energy of 5 KeV. The chemical state analysis by ESCA for the fume generated from the combustion of Montana lignite (45/53 um) in twenty percent oxygen in nitrogen at a furnace temperature of 1750 K is presented in chapter six.

Despite the fact that sputtering is a widely accepted technique for obtaining elemental depth profiles, care should be used in the interpretation of the results from the sputtering depth profile due to sputtering artifacts, where certain species can be preferential sputtered (Andersen and Hathorne, 1972; Sigmund, 1969).
Figure 4.10 - Auger spectra of Mg and MgO (Davis et. al., 1976)
Table 4.9 - Relative sensitivity factors obtained experimentally (Ep = 5.0 KeV)

<table>
<thead>
<tr>
<th>element</th>
<th>electron energy (eV)</th>
<th>$S_{x/Ag}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>LMM 152</td>
<td>0.724</td>
</tr>
<tr>
<td>S</td>
<td>KLL 2117</td>
<td>0.0138</td>
</tr>
<tr>
<td>Si</td>
<td>LMM 76</td>
<td>0.084</td>
</tr>
<tr>
<td>Si</td>
<td>KLL 1606</td>
<td>0.367</td>
</tr>
<tr>
<td>Mg</td>
<td>LMM 32</td>
<td>0.164</td>
</tr>
<tr>
<td>Mg</td>
<td>KLL 1174</td>
<td>0.246</td>
</tr>
<tr>
<td>Na</td>
<td>KLL 990</td>
<td>0.25</td>
</tr>
<tr>
<td>K</td>
<td>KLL 252</td>
<td>0.90</td>
</tr>
<tr>
<td>Ca</td>
<td>KLL 291</td>
<td>0.478</td>
</tr>
<tr>
<td>Fe</td>
<td>KLL 703</td>
<td>0.21</td>
</tr>
</tbody>
</table>
4.7 ESCA

Electron spectroscopy for chemical analysis (ESCA) was used to determine the chemical state of the inorganic species. The system used was a PHI 548 ESCA/Auger unit with a precision electron analyzer. The analyzer, a double pass cylindrical mirror analyzer with retarding grid input, measures the kinetic energy of the photoelectron. The excitation source is a magnesium anode which produces monochromatic Mg k alfa x-rays at 1253.6 eV with a source of 400 watts. The sample chamber during analysis is maintained below $10^{-9}$ Torr.

In ESCA, the specimen is excited with monochromatic x-ray beam. In returning to their ground state, these atoms eject photoelectrons, whose measure kinetic energy is defined by

$$KE = hv - BE - Os$$  \hspace{1cm} \text{Eq. 4.9}

where $hv$ is the energy of the incident photon, $BE$ is the binding energy of the electron in the orbital state from which the electron originated, $Os$ is the spectrometer work function, and $KE$ is the kinetic energy of the emitted electron. Using this relation, binding energies can be calculated once the energy of the exciting x-rays and the emitted electron's kinetic energy are known. In theory, when the binding energies are known, chemical state information
can be deduced, since the binding energy (how tightly they are held to their respective atoms) is sensitive to the chemical state. In general, identification of the oxidation state can be easily determined since measurable differences in the binding energy (> 1.0 eV) exist for the various oxidation states. On the other hand, differentiation between the various compounds is limited, since the difference in the resulting shift maybe small (< 1.0 eV).

The identification of chemical state depends primarily on the accurate determination of the binding energies. To determine binding energies accurately, a peak with narrow sweep range must be recorded with good statistics, and accurate correction must be made for insulating specimen when static charging is present.

During analysis, insulating samples tend to acquire a steady state charge. This steady state charge is a balance between electron loss from the surface by emission and electron gain by conduction or by acquisition of slow thermal electrons from the vacuum space. A serious problem is the exact determination of the extent of charge shifting. The steady state charge, usually positive, adds to the retardation of the photoelectron and tends to make peak appear at higher binding energy. Charging can shift peak location by more than 2 eV as well as affecting the shape of the peak.

The method for valid charge correction for insulating
samples is to reference the carbon Cls line (284.6 eV) of the adventitious hydrocarbon present on the sample's surface. Any shift in the Cls peak from the 284.6 eV value can be taken as a measure of the static charge. An example of the charge correction procedure is presented in Figure 4.11. Verification of the measured extent of static charge shifting can be obtained by establishing the chemical state for at least one of the species by an independent method (ie., mossbauer, x-ray diffraction, and Auger spectroscopy).

Instrumental calibration is essential for quantitative analysis. To eliminate problems arising from charging, conductive samples were employed for the spectrometer calibration. The first analysis established a linearity problem with the electronics, where the deviation in apparent binding energies (ie., measured) from the referenced binding energies for three conductive standards (eg., Cu, Ag, and Pt) increased with increasing binding energy. After realignment of the spectrometer, the deviation was within two tenths of an eV, Table 4.10.

After correcting for static charge shifting, the chemical state of inorganic species in the fume were determined by comparing the apparent binding energy to the reference binding energies compiled by PHI (Wagner et. al., 79). Conformation for chemical state identification was obtained by checking the reference binding energies with our own standards, Table 4.11. The error in the peak location
Figure 4.11 - ESCA high resolution scan of carbon C 1s line for fume sample

Charge Shift of 2.7 eV

A - Measured carbon peak (287.3 eV)
B - Reference C 1s line (284.6 eV)
Table 4.10 - Calibration of ESCA spectrometer with Au, Ag, and Cu metal standards

<table>
<thead>
<tr>
<th>standard</th>
<th>peak</th>
<th>apparent binding energy</th>
<th>reference binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>$4f_{7/2}$</td>
<td>83.8</td>
<td>84.0</td>
</tr>
<tr>
<td>Ag</td>
<td>1s</td>
<td>367.9</td>
<td>367.9</td>
</tr>
<tr>
<td>Cu</td>
<td>$2p_3$</td>
<td>932.4</td>
<td>932.4</td>
</tr>
<tr>
<td>element</td>
<td>compound</td>
<td>Standard's binding energy (eV)</td>
<td>reference binding energy (eV)</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td>--------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>Mg (2p)</td>
<td>MgO</td>
<td>49.4</td>
<td>51.6 *</td>
</tr>
<tr>
<td>Fe (2p_{3/2})</td>
<td>Fe_{3}O_{4}</td>
<td>---</td>
<td>711.4</td>
</tr>
<tr>
<td>Si (2p)</td>
<td>SiO_{2}</td>
<td>103.1</td>
<td>103.4</td>
</tr>
<tr>
<td>S (2p)</td>
<td>Na_{2}SO_{4}</td>
<td>168.8</td>
<td>168.6</td>
</tr>
<tr>
<td>Na (1s)</td>
<td>Na_{2}SO_{4}</td>
<td>1071.2</td>
<td>1071.3</td>
</tr>
<tr>
<td>Ca (1s)</td>
<td>CaO</td>
<td>347.4</td>
<td>346.3 *</td>
</tr>
</tbody>
</table>

* Castleton (81) also disputes PHI B.E.
for Mg and Ca for the spectra compiled by PHI (Wagner et al., 1979) has been confirmed from work conducted at the DOE research facility, METC (Castleton, 1981).
CHAPTER FIVE
FACTORS INFLUENCING THE BULK CHARACTERISTICS
OF THE SUBMICRON PARTICLES

The experimental basis of this investigation was to combust a dilute stream of pulverized coal particles under well controlled conditions in the drop tube laminar flow furnace. For the carefully controlled combustion conditions, the important variables which govern the physico-chemical characteristics of the submicron particles were examined. Specifically, the influence of the combustion condition, residence time, and coal type on mass loading, particle size distribution (PSD), particle morphology, and bulk chemical composition of the submicron particles were examined.

5.1 FLY ASH MASS DISTRIBUTION

The mass distribution of the particulate combustion products (i.e., fly ash) on the cascade impactor stages and final filter (FF) from the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen are presented in Figure 5.1. The mass distribution of the fly ash was obtained by weight analysis of the various impactor stages and final filter. The weights are based on one gram of coal burned. Clearly, the bulk of the mass is collected in the preseparator (stage 0)
Figure 5.1 - Mass distribution of particulate combustion products on cascade impactor stages and final filter.
where the aerodynamic diameters of the particles are greater than 11.5 microns. The mass decreases successively with decreasing particle size where less than three tenths of a percent of the mass is collected on the final stages (stages 6 and 7). The particles collected on the various impactor stages are referred to as the residual fly ash which are produced by fusion and coalescence of the mineral inclusions in each coal particle during combustion. The variation in ash particle size, which is considerably greater than that of the parent coal particle, is attributed to differences in ash content of individual coal particles, to fragmentation of coal particles during combustion, and to cenosphere formation by the ash (Ramsden, 1969; Sarofim et. al., 1977; Raask and Williams, 1965; and Raask, 1966). There is a significant increase in the amount of material collected on the final filter relative to stages 6 and 7 which reflects the bimodal nature of the fly ash previously observed in field studies (Marcowski et. al., 1980; McCain et. al., 1975). The submicron mode is believed to be formed from the condensation of the inorganic vapors, which pass through the entire cascade impactor and collect on the final filter because of their small size with aerodynamic diameters of less than 0.5 microns.

The fly ash mass distributions obtained from the cascade impactor for various combustion conditions where the main gas oxygen partial pressure was varied from ten percent
to sixty six percent for the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K, are presented in Figure 5.2. The relative mass loading on the various stages depends only weakly on the combustion conditions (i.e., oxygen partial pressure) where a slight shift in mass loading to the lower impactor stages with increasing oxygen partial pressure is observed. On the other hand, the mass loading on the final filter is extremely sensitive to the specific combustion conditions where the amount of material collecting on the final filter increases over an order of magnitude as the oxygen partial pressure is increased from ten percent to sixty six percent.

Transmission electron micrographs of the material collecting on the final filter are presented in Figure 5.3 for the combustion of Montana lignite (45/53 microns) in 10, 20, and 40 percent oxygen in nitrogen. The samples were prepared for the TEM by depositing the submicron particles on TEM grids placed in the electrostatic precipitator down stream from the cascade impactor. The particles collecting on the final filter are as anticipated extremely small, less than 1000 angstroms in diameter. Under these conditions the existence of clustered and chained agglomerates, which are composed on the average of three to four discrete spherical particles, is observed. The average primary particle size increases with increasing oxygen partial pressure. For low oxygen partial pressures where the mass loading is small, the
Figure 5.2 - Distribution of particulate combustion products for various combustion conditions
Figure 5.3 - Fume particles produced from the combustion of Montana lignite in 40 (A), 20 (B), and 10 (C) percent oxygen in nitrogen.
The presence of many transparent particles made visible in transmission by their faint haloes is observed, Figure 5.3 (C). The faint haloes have been identified by their morphology as sulfuric acid mist (Frank and Lodge, 1967). As the oxygen partial pressure is increased (i.e., increase in mass loading), the observed presence of sulfuric acid mist diminishes where above oxygen partial pressure of fifteen percent the presence of the sulfuric acid mist is not observed. For low oxygen partial pressures, the simultaneous collection of sulfuric acid mist with the inorganic submicron particles on the final filter raises concern about the integrity of the inorganic particles in this reactive environment. The collection efficiency for sulfuric acid mist has been shown to be highly dependent on the filtration temperature and the gas flow rate (i.e., contact time) (Cheney et. al., 1979). The collection of sulfuric acid mist can be eliminated by maintaining the filtration temperature above 323 K for gas flow rates above $1.7 \times 10^4$ m$^3$/sec. The relatively low filtration temperature (i.e., dew point) results from the dilution of the combustion products (e.g., SO$_3$ and H$_2$O) by the quench gas upon sampling. Consequently, all samples being prepared for chemical analysis will be collected under those conditions in order to alleviate concern about anomalies in the analysis due to sampling artifacts.

The volume-mean diameter of the primary submicron
particles produced under various combustion conditions where the main gas oxygen partial pressure was varied from ten to seventy five percent for the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K is shown in Figure 5.4. The volume-mean diameter of the primary submicron particles was obtained from TEM micrographs by an automated image analyzer where between 200 and a 1000 particles were sized for each condition. As previously noted, the volume-mean diameter of the submicron particles increases with increasing oxygen partial pressure (i.e., increase in mass loading of fume).

The volume distributions of particles in the submicron range (i.e., those particles collected on the final filter) and on various impactor stages for the combustion of Montana lignite (45/53 um) in fifteen and forty percent oxygen in nitrogen are shown in Figure 5.5. The actual volume-mean diameters of the particles at stages one through seven, were used. The determination of the actual volume-mean diameters for each of the stages is discussed in section 3.4. The actual volume distribution of the particles collected in the preseparator is presented in order to illustrate the distribution of the residual fly ash particles greater than 5.65 microns. The distinct separation between the residual fly ash mode and the submicron particulate mode clearly demonstrates the bimodal nature of fly ash formed from the direct combustion of pulverized coal particles.
Figure 5.4 - Volume-mean diameter of submicron primary particles for various oxygen partial pressure
Figure 5.5 - Particle size distribution of particulate combustion products

Montana lignite fly ash PSD

- 15% O₂/N₂
- 40% O₂/N₂
Comparison of the distributions for the two combustion conditions clearly illustrated the sensitivity of the total mass loading and volume mean diameter of the submicron mode to the combustion condition.

5.2 BULK CHEMICAL COMPOSITION

The composition of the major oxides in the fume produced under various combustion conditions where the main gas oxygen partial pressure was varied from ten percent to fifty percent for the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K is shown in Figure 5.6. The concentration of the major oxides were determined by INAA, AA, and liquid chromatography. At higher oxygen partial pressures the refractory oxides, MgO and CaO, accounts for most of the mass, while at low oxygen partial pressures the volatile species Na2O accounts for significant fraction of the mass of the particles. Despite the fact that the concentration of sulfur in the fume decreases with increasing oxygen partial pressure, the relative retention of sulfur in the fume increases from one to six percent, Figure 5.7. Since the rate of oxidation of SO$_2$ to SO$_3$ is extremely slow, the increase in the formation of stable inorganic sulfate with increasing amount of fume appears to account for the observed decrease in the amount of sulfuric acid mist at ambient temperatures.

The concentration of the major, minor, and trace
Figure 5.6 - Variation of composition of the fume for various combustion conditions.
Figure 5.7 - Sulfur retention in the fume
inorganic elements are given in Table 5.1 for the coals: Montana lignite, North Dakota lignite, Alabama Rosa, and Pittsburgh No 8. The major, minor, and trace metal content of the different coals do vary. From detailed characterization of the mineral matter (Quann, 1982), the coals were found to contain discrete mineral phases such as quartz $[\text{SiO}_2]$, kaolinite $[\text{Al}_2\text{SiO}_5(\text{OH})_4]$, pyrite $[\text{FeS}]$, calcite $[\text{CaCO}_3]$, and dolomite $[\text{MgCa(CO}_3]_2]$. The trace elements can occur as either impurities in the major mineral forms as discrete mineral phases in extremely small quantities or as chelated compounds in the organic matter of the coal. In the high rank bituminous coals, the mineral phases occur as micron sized mineral inclusions embedded in the carbonaceous matrix. By contrast, the alkaline earth metals in the low rank lignites are not present to any extent as discrete mineral phases but rather as an intimate part of the chemical structure of the coal. More precisely, they occur in ion exchanged form on carboxyl and phenolic function groups.

The amount and composition of the fumes produced from the combustion of each of the coals at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen are given in Table 5.2. The amount and concentration of the fume vary much more dramatically than anticipated from the variation among the original coals. For the bituminous coals, the amount of fume produced is less than that for the low rank coals, particularly the high sodium containing North Dakato
TABLE 5.1 - Coal composition for major, minor, and trace elements

<table>
<thead>
<tr>
<th>element</th>
<th>MS(L)</th>
<th>ND(L)</th>
<th>AL(B)</th>
<th>PT#8(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.61</td>
<td>0.31</td>
<td>----</td>
<td>0.073</td>
</tr>
<tr>
<td>Si</td>
<td>0.75</td>
<td>0.55</td>
<td>1.65</td>
<td>1.36</td>
</tr>
<tr>
<td>Al</td>
<td>0.71</td>
<td>0.41</td>
<td>0.66</td>
<td>0.88</td>
</tr>
<tr>
<td>Ca</td>
<td>1.72</td>
<td>1.13</td>
<td>----</td>
<td>0.59</td>
</tr>
<tr>
<td>Fe</td>
<td>0.20</td>
<td>0.49</td>
<td>0.36</td>
<td>0.89</td>
</tr>
<tr>
<td>S</td>
<td>0.55</td>
<td>0.55</td>
<td>0.77</td>
<td>2.83</td>
</tr>
</tbody>
</table>

parts per million

<table>
<thead>
<tr>
<th>element</th>
<th>Na</th>
<th>K</th>
<th>As</th>
<th>Zn</th>
<th>Cr</th>
<th>Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250.0</td>
<td>300.0</td>
<td>4.0</td>
<td>11.0</td>
<td>7.5</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>7360.0</td>
<td>300.0</td>
<td>3.4</td>
<td>62.0</td>
<td>16.0</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>330.0</td>
<td>1700.0</td>
<td>21.0</td>
<td>&lt;10.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

ASTM ash* | 7.5 | 6.9 | 7.1 | 7.4 |

* weight percent
Table 5.2 - Submicron fume composition

<table>
<thead>
<tr>
<th>element</th>
<th>MS(L)</th>
<th>ND(L)</th>
<th>Al(B)</th>
<th>Pt#8(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>59.9</td>
<td>13.3</td>
<td>0.6</td>
<td>3.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.6</td>
<td>1.4</td>
<td>22.6</td>
<td>46.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.4</td>
<td>0.1</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>CaO</td>
<td>8.9</td>
<td>2.7</td>
<td>1.07</td>
<td>1.5</td>
</tr>
<tr>
<td>FeO</td>
<td>12.4</td>
<td>14.3</td>
<td>54.5</td>
<td>20.9</td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.3</td>
<td>38.4</td>
<td>9.4</td>
<td>13.9</td>
</tr>
<tr>
<td>SO₃</td>
<td>6.6</td>
<td>29.8</td>
<td>5.6</td>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
</tr>
<tr>
<td>Zn</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Sc</td>
</tr>
</tbody>
</table>

Percent of ASTM ash

|                | 2.86 | 8.85 | 1.63 | 1.56 |
The fume from the bituminous coals are dominated by silicon and iron while in contrast the fumes from the low rank coals have significant and dominant amounts of magnesium and calcium in addition to iron. The fume of North Dakota lignite is mostly composed of sodium. The sulfur retention for the high sodium fume of North Dakota lignite is over thirty percent while for the relatively low sodium fume of Alabama rosa, the sulfur retention is below one percent. The sulfur content in the various fumes correlates fairly well with the sodium and potassium content in each of the fumes examined, Figure 5.8.

The combustion conditions have been shown to greatly influence the nature of the particulate combustion products where the amount, composition, and size of the submicron particles are extremely sensitive to combustion condition. In order to facilitate a better understanding, the combustion process will be reviewed.

5.3 COMBUSTION TEMPERATURE TIME HISTORY

Extensive theoretical and experimental efforts have been devoted to the subject of pulverized coal combustion (Field et. al., 1967; Smith, 1978). Under the combustion conditions being investigated, where the coal particles are less than 150 microns in diameter and the particle combustion temperatures are above 1600 K, the rate of combustion will be externally diffusion limited. Therefore, the temperature
Figure 5.8 - Comparison of S to Na and K in the fume
time history of the burning char particle will be highly dependent on the oxygen partial pressure in the bulk gas phase.

The combustion temperature-time history for Montana lignite particles will be determined experimentally by two color optical pyrometry. The principle and application of this technique to the combustion furnace is discussed elsewhere in greater detail (Timothy, 82; Altrichter, 81). Briefly, a slightly modified feeding system is employed where single particles can be fed individually. This will allow the measurement of the temperature of single coal particles from ignition to burnout. The temperature-time data to be presented was obtained from the investigations by Dictor (1979), Altrichter (1980), and Timothy (1981) where the particle burning times were obtained simultaneously with particle temperature measurements for single coal particles.

Temperature measurements by two color optical pyrometry were obtained for individual Montana lignite particles in oxygen partial pressures greater than fifteen percent, Figure 5.9. At each condition, fifteen to twenty individual particles were examined. At lower oxygen partial pressures the light emitted from the burning particle was of insufficient intensity for photomultiplier detection. Consequently, at extremely low oxygen partial pressure the particle combustion temperatures were assumed to approach the bulk gas temperatures. As evident, increasing the oxygen partial
Figure 5.9 - Average particle temperature of Montana lignite (90/105 μm) by two color pyrometry.
pressure results in an increase in the combustion temperature of the coal particles. The particle combustion temperature exceeds the bulk gas temperature due to the heat released from the highly exothermic heterogeneous oxidation reaction occurring at the surface of the particle. For low oxygen partial pressure in argon the particle combustion temperature is extremely sensitive to variation in oxygen partial pressure. However, at high oxygen partial pressures the increase in the particle combustion temperature is more gradual with increasing oxygen partial pressure. This has been attributed to the high temperature dissociation of the gases in the particle boundary layer which enhances the heat transfer away from the burning char particle (Sarofim, 1979). For the two furnace temperatures examined (e.g., 1700 K and 1250 K), the characteristic trends in the particle combustion temperatures with oxygen partial pressure are similar while the magnitude of the particle temperatures achieved during combustion is shown to be dependent on the furnace temperature.

The average time elapsed between ignition and burnout of 90/105 micron Montana lignite particles for oxygen partial pressures from ten to one hundred percent are shown in Figure 5.10. The various studies qualitatively display the same response: as the oxygen partial pressure decreases the total burning time of the particle increases. For external diffusion limited combustion of non-swelling coals such as
Figure 5.10 - Burning time for Montana lignite (90/105 μm)
Montana lignite the burning time should be governed by the relations

\[ t_b = \frac{24 \, \text{cw} \, D_{O_2} \, d_0^2 \, p_0 \, \rho \, \ln (1 + X_{O_2})}{D_{O_2}} \]  

Eq. 5.1

where \( t_b \) is the total burning time, \( p \) is the particle density with respect to carbon content, \( D_{O_2} \) is the diffusion coefficient for \( O_2 \), and \( X_{O_2} \) is the mole fraction of oxygen. As evident, a linear correlation of \( d_0^2 / t_b \) with \( \ln (1 + X_{O_2}) \) is obtained, Figure 5.11, indicating external diffusion limited combustion. The burning times for Montana lignite at a given oxygen partial pressure will proportional to the square of the initial particle diameters. The main gas temperature does not appear to have significant effect on burning time as seen from the comparison of the burning times between Timothy with a main gas temperature of 1250 K and Alterichter at 1640 K.

The temperature/time history for the single particle feed experiments by two color optical pyrometry are assumed to apply to the combustion of particles in the dilute cloud experiment. From those studies, the temperature/time history for the combustion of Montana lignite has been shown to be highly dependent on the oxygen partial pressure. Increasing the oxygen partial pressure in the main gas results in a corresponding increase in combustion rate and temperature of burning coal particle. The focus of the next section will examine the mechanism of ash vaporization, the extent of
Figure 5.11 - Reciprocal of burning time verse $\ln(1 + X_0)$
which will be highly sensitive to the temperature/time history of the mineral constituents associated with the char particle. Since the submicron particles are formed from the volatilized inorganics, the vaporization mechanisms should establish the influence that the combustion conditions and coal type have on the ultimate composition, amount, and size of the submicron particles.

5.4 VAPORIZATION

It has been proposed that the determination of the elements in the fume, that material which is collected on the final filter, should prove to be a sensitive measure of the degree of ash vaporization, since the submicron particles are formed from the condensation of the vaporized ash (Quann, 1982).

The fraction of the total ash and the constituent elements appearing on the final filter for various combustion conditions where the oxygen partial pressure is varied from six to fifty percent oxygen for the combustion of Montana lignite (45/53 um) at furnace temperature 1700 K, is shown in Figure 5.12. The fraction of refractory constituents Mg, Al, Ca, Si, Fe and Sc appearing in the fume increase over an order of magnitude as the oxygen partial pressure (i.e., particle combustion temperature) is increased from six to fifty percent. In contrast, the volatile constituents As, Na, and Sb show only a slight dependence on oxygen partial
Figure 5.12 - Dependence on oxygen partial pressure of elemental and ash fraction in fume
pressure where the fraction of these elements appearing in the fume is relatively high (> forty percent). Under the combustion conditions examined, the volatile trace species should have totally vaporized due to their high vapor pressure. The discrepancy between the amount of the volatile species appearing on the final filter and that in the parent coal may be attributed to the fact that some of these volatile species will heterogeneous condensation on the surface of the larger ash particles. Evidence for the heterogeneous condensation of the volatile species on the surface of the residual fly ash particles can be obtained by examining the dependence of their concentration on particle size. Size classified samples of the residual fly ash particles for chemical analysis by INAA were obtained by using the cascade impactor. The concentration of some of the typical species on the various stages of the cascade impactor and final filter are shown in Figure 5.13. The concentration of those species in the overall ash are shown on the right axis. The concentration of magnesium, calcium, iron, alumina, and scandium show no systematic variation with particle size. On the other hand, the volatile trace species such as arsenic, antimony, and sodium all show pronounced increasing concentration trends with decreasing particle size. Relative to the parent ash, the concentration of arsenic, antimony, and sodium in the larger particles are depleted while the smaller ones are highly enriched. The observed increase in concentration for sodium, arsenic, and antimony with decreasing
Figure 5.13 - Variation of elemental mass fraction with particle size for the residual fly ash
particle size suggest that these species condense heterogeneously on the surface of the residual fly ash. (Davison et. al., 1974; Ondov et. al., 1979; and Smith et. al., 1979). The concentration trends for the volatile element arsenic in the residual fly ash produced from the combustion of Montana lignite (45/53 um) in 5, 10, 20, and 50 percent oxygen are shown in Figure 5.14. The observed concentration trends for the different combustion conditions are best correlated with inverse diameter. As the amount of fume produced is increased, the slope of the concentration of arsenic with particle diameter is less accentuated. This coincides with the increase in the amount of arsenic collected in the fume, Figure 5.12. The parallel and competing paths for the deposition of the volatile species in the two modes of the fly ash (e.g., residual and submicron) will be examined in chapter seven. The determination of the degree of vaporization and hence the rate of vaporization will be restricted to the refractory species.

The details of vaporization of the various mineral constituents have been investigated in a complimentary study by R. Quann (1982). The finding from his investigation have established; (1) the vaporization rate is controlled by internal and external vapor transport processes; (2) the volatilization of the refractory oxides is enhanced by their chemical reduction to their more volatile suboxide (SiO) or metal (Mg) vapors due to the extremely reducing environment.
Figure 5.14 - Concentration of As in sized classified residual fly ash particles
found within the burning char particle; (3) the overall rate of vaporization will be dependent on the original coal particle size, the degree of dispersion of the mineral forms (extraneous, inherent micron size inclusion, or atomically dispersed within carbon matrix), and on the mineral forms present in the specific coal (e.g., quartzs vs Kaolinite for silicon).

The rate expression for external diffusion limited vaporization can be derived from Fick's first law:

$$\frac{dn_i}{dt} = \frac{2 \pi D_i}{RT} \frac{d_p(t)}{d_i} p_s(T_p) \quad \text{Eq. 5.2}$$

where $p_s(T_p)$ is the vapor pressure at the char surface, $T_p$ is the particle temperature, $n_i$ is the number of moles vaporized from the single particle, $D_i$ is the diffusivity of $i$, and $d_p(t)$ is the char particle diameter at time $t$. For nonswelling coals which is the case for Montana lignite coal, the burning char particle is modeled as a shrinking sphere with the time dependence

$$d_p(t) = d_o \left(1 - \frac{t}{t_b}\right)^{1/2} \quad \text{Eq. 5.3}$$

where $d_o$ is the initial diameter and $t_b$ is the burning time of the char particle. In substituting the time dependence relationship for char particle size, equation 5.2 can be integrated over the total burning time. The fraction vaporized is
\[ \phi(t_b) = \frac{8 D_i P_s(T_p) t_b}{C_0 R T d_o^2} \quad \text{Eq. 5.4} \]

where \( C_0 \) is now the initial volume concentration of species \( i \) in the particle. Assuming a Clausius–Clapeyron temperature dependence of the vapor pressure, the fraction vaporized will have the following temperature dependence.

\[ \frac{d\ln \phi(t_b)}{dt_b} \sim \frac{dH_{vap}}{R} \quad \text{Eq. 5.5} \]

where \( H_{vap} \) is the heat of vaporization. For externally diffusion limited vaporization, the log of the vaporization rate (extent vaporized per unit time) should be inversely proportional to particle temperature. As evident in Figure 5.15, a linear relationship is obtained between the log of the rate of vaporization versus particle combustion temperature for Mg, Al, Si, Ca, Fe, and Sc where the burning time and average particle temperature were obtained from two color optical pyrometry studies. At conventional combustion temperatures (~2000 K) the rate of vaporization increases in the sequence Al, Ca, Fe, and Mg where the relative rates span over three orders of magnitude.

Time-resolved measurements of the ash vaporized by Quann (1982) are shown in Figure 5.16. In these experiments, Montana lignite (nominal 140 micron diameter) was burned in
Figure 5.15 – Temperature dependence of the elemental vaporization rates
Figure 5.16 - Time-resolved profiles of maximum yield of char and submicron particle constituents
thirty percent oxygen in nitrogen at a furnace temperature of 1750 K. The position of the collection probe was adjusted to quench the char particle combustion process at successive stages of burnout. Weight loss measurements were used to determine the extent of burnout at each position. The fraction of ash vaporized was determined from the amount of fume collected on the final filter of the cascade impactor at each residence time. During the first 100 milliseconds, the coal is heated to the furnace temperature. After this initial period, the char particles ignite and burn to completion at about 12.5 cm. The data demonstrate that the ash vaporizes only during the char combustion process. This is expected because it is during this period that the ash experiences the locally reducing atmosphere within the char and the temperature overshoot caused by the exothermic char combustion reaction. It is of note that in the post combustion period there is no measurable change in the mass of submicron material.

For the time resolve vaporization study, the variation in primary particle size was examined, Figure 5.17. The submicron particles are shown to form at the onset of char combustion, where their size increases very rapidly with position.

The vaporization characteristics of the inorganic elements which are dependent on both the combustion conditions and coal type ultimately determine the amount, size,
Figure 5.17 - Time resolve measurements of the mean primary particle radius for the submicron particles.
and composition of the submicron particles. The amount of fume produced depends on the combustion temperature/time history and the characteristics of the mineral forms since the extent of vaporization has been shown to be dependent on these two parameters. The large contribution of the refractory oxides which account for the bulk of the fume is attributed to the enhanced vaporization of the refractory oxides by their chemical reduction to the more volatile suboxide or metal due to the reducing environment found within the char particle during combustion. The fume composition from different coals vary to a greater degree than in the overall ash as a result of the influence of the differences in the degree of dispersion of the inorganics and type of mineral forms present.
The following investigation examined the chemistry of the inorganic submicron particles formed from the combustion of Montana lignite (45/53 μm) at furnace temperature of 1700 K in twenty percent oxygen in nitrogen. With the development of the analytical capabilities of the scanning transmission electron microscope (STEM), ESCA, Auger spectroscopy, and INAA detailed information about the dependence of concentration on particle size, the elemental composition of the individual primary particles, the elemental stratification within the submicron particle, and the chemical state of the major elements was determined.

6.1 BULK COMPOSITION

The average bulk particle concentration by INAA, AA (K₂O and SiO₂), and liquid chromatography (SO₃) of four separate fume samples is presented in Table 6.1. The concentration of those species in the overall ash, calculated from the coal composition with an ash content of 7.1 percent is also presented in Table 6.1. All the elements are presented in their highest oxidation state. The dominant constituents of the submicron particles are the refractory oxides of
Table 6.1 Chemical analysis of the submicron particles produced from the combustion of Montana lignite (45/53 um) at furnace temperature of 1750 K in twenty percent oxygen in nitrogen.

<table>
<thead>
<tr>
<th>element</th>
<th>weight percent</th>
<th>parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>59.9</td>
<td>375.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.6</td>
<td>1140.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.4</td>
<td>360.0</td>
</tr>
<tr>
<td>CaO</td>
<td>8.9</td>
<td>0.8</td>
</tr>
<tr>
<td>FeO</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>2.86</td>
<td></td>
</tr>
</tbody>
</table>

Percent of ASTM ash
magnesium (56 percent), calcium (10 percent), and iron (8.0 percent). The trace volatile species such as arsenic, antimony, and sodium are highly enriched in the submicron particles, having a concentration of over two order of magnitude greater than that in the overall ash. When the weight of the material collected on the final filter was compared with the amount determined by chemical analysis (i.e., oxide weight), approximately fifteen percent of the weight could not be accounted for. The hydroscopic nature of the fume with its extremely high surface area (i.e., 133.0 m$^2$/g), makes the adsorption of water unavoidable (Rothenberg and Cheng, 1980). Repetitive drying experiments showed that the dry weight of the material on the final filter coincided with the weight of the oxides. When the dry filter was exposed to the room environment, the filter sample regained its original weight within ten minutes. The drying experiments suggested the presence of adsorbed water, and thus it can be assumed that the total amount of material collected on the filter is now accounted for.

6.2 DEPENDENCE OF CONCENTRATION ON PARTICLE SIZE

Size classified samples of the submicron particles for chemical analysis by INAA were obtained with the mobility classifier. The chemical composition of the individual submicron particles were obtained from microprobe analysis by the STEM.
Four discrete size cuts of the submicron particles with mean particle diameter of 100, 200, 300, and 400 angstroms were obtained with the mobility classifier. The relative concentration of Mg, Ca, Fe, Al, Na, Sb, and As in each of the four size cuts are shown in Figure 6.1 and Figure 6.2. Sodium, arsenic, chromium, antimony, and aluminum all show increasing concentration trends with decreasing particle size. Iron, and calcium show no systematic variation in concentration with particle size, while magnesium shows a slight decrease in concentration with decreasing particle size.

The STEM's capability for microprobe analysis provides for the first time detailed information about the composition of individual submicron particles. As previously mentioned in section 4.5, only those stable species (i.e., Si, Mg, Fe, and Ca) whose x-ray signals remain constant over time under the high intensity electron beam, will be examined. Microprobe analysis of the primary submicron particles, with diameters ranging between eighty and four hundred angstroms were choosen at random. Figure 6.3 shows the elemental concentration for the various primary particles. There is no major trend in the concentration of magnesium, calcium, and iron with particle size. However, magnesium and iron do show a slight variation in concentration from particle to particle, while calcium concentration is relatively constant. Silicon, on the other hand, exhibits
Figure 6.1 - Elemental concentration for size classified samples by INAA
Figure 6.2 - Elemental concentration for size classified samples by INAA
Figure 6.3 - Elemental concentration for primary particles by STEM
a marked increase in concentration with decreasing particle size. Results showing the concentration trends for calcium, iron, and magnesium with particle size by STEM analysis of individual particles and by INAA of sized classified samples of a large number of particles are in agreement.

The observed increase in concentration with decreasing particle size for Na, As, Sb, Al, and Si is hypothesized to result from heterogeneous condensation of these elements on the surface of the pre-existing particles composed of magnesium, iron, and calcium. The concentration trends result from the fact that the surface to volume ratio increases with decreasing particle size.

The microprobe analysis of submicron particles formed from the combustion of Montana lignite (120/150 um) in seventy five percent oxygen shows a dramatic variation in the composition irrespective of particle size, Table 6.2. The relative concentration of silicon, calcium, magnesium, and iron in the bulk fume sample as determined by INAA and AA are also shown in Table 6.2. A large number of the primary particles are highly enriched in either silicon (98 percent), calcium (86 percent), or magnesium (76 percent), while the remaining particles have unusually high iron content (43 percent). The analysis suggests that these species might selectively condense, forming relatively pure particles of silicon, magnesium, calcium, and iron where the presence of other constituents in each particle is due to subsequent
Table 6.2 STEM microprobe analysis of individual submicron particles produced from the combustion of Montana lignite (150 μm) at furnace temperature of 1700 K in seventy five percent oxygen.

<table>
<thead>
<tr>
<th>particle diameter Å</th>
<th>SiO$_2$ (wt%)</th>
<th>CaO (wt%)</th>
<th>MgO (wt%)</th>
<th>FeO (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>11</td>
<td>8</td>
<td>66</td>
<td>15</td>
</tr>
<tr>
<td>140</td>
<td>7</td>
<td>1</td>
<td>51</td>
<td>32</td>
</tr>
<tr>
<td>250</td>
<td>92</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>300</td>
<td>55</td>
<td>1</td>
<td>1</td>
<td>43</td>
</tr>
<tr>
<td>350</td>
<td>98</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>425</td>
<td>7</td>
<td>23</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>450</td>
<td>5</td>
<td>14</td>
<td>75</td>
<td>6</td>
</tr>
<tr>
<td>480</td>
<td>4</td>
<td>86</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

bulk fume conc.*    10 52 35 3

* by INAA and AA
heterogeneous condensation and coagulation between relatively pure particles.

6.3 SURFACE ENRICHMENT

The elemental stratification in the submicron particle was determined by: (1) comparing the surface concentration, measured by Auger spectroscopy, with bulk particle concentration measured by INAA, AA, and liquid chromatography; (2) determining the variation in concentration measured by Auger spectroscopy as the surface layers are sputtered away; and (3) comparing the ratio of the intensity of the high and low energy Auger electrons emitted from the sample to the ratio for a homogeneous bulk standard.

The surface concentration by Auger spectroscopy is compared in Table 6.3 with the bulk particle concentration by INAA (Na$_2$O, MgO, CaO, and FeO), AA (K$_2$O, and SiO$_2$), and liquid chromatography (SO$_3$). All elements are reported as their oxides for convenience. A comparison of the two analyses shows that sodium, sulfur, potassium, and silicon are highly concentrated in the surface layers, while conversely magnesium and iron are depleted. From the comparison of the two analyses, calcium is neither highly concentrated nor depleted in the surface layers.

In order to obtain the concentration as a function of depth from the surface, the fume sample was sputtered at a milling rate that corresponds to a surface regression rate of
Table 6.3 Auger spectroscopy of the fume produced from the combustion of Montana lignite (45/53 um) at furnace temperature of 1700 K in twenty percent oxygen in nitrogen.

<table>
<thead>
<tr>
<th>species</th>
<th>surface conc. (Auger) (wt%)</th>
<th>bulk conc. (INAA)* (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>11.8</td>
<td>5.3</td>
</tr>
<tr>
<td>SO₃</td>
<td>16.4</td>
<td>7.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.6</td>
<td>1.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>14.9</td>
<td>3.5</td>
</tr>
<tr>
<td>CaO</td>
<td>12.3</td>
<td>9.7</td>
</tr>
<tr>
<td>MgO</td>
<td>29.3</td>
<td>58.6</td>
</tr>
<tr>
<td>FeO</td>
<td>3.9</td>
<td>11.8</td>
</tr>
</tbody>
</table>

* supplemented with AA and liquid chromatography
about twenty five angstroms per minute for a Te2O5 sputtering standard (Martin, 1980). Auger analyses of the original surface and at several sputtered times are presented in Table 6.4. The concentration of species in which the surface is enriched, such as sodium, sulfur, and potassium decreases with extent of sputtering, while species in which the surface is depleted, such as magnesium and iron, increase proportionally. The relative concentration of calcium with successive sputtering remains constant, suggesting that calcium is present near the surface as well as in the core of the particle. The asymptotic concentration shows a significant contribution from the surface enriched species. This is unavoidable since the emission for a sectioned particle will always include contributions from surface layers, Figure 6.4 (A). This is compounded by the nature of the sample's surface topography, since the ion sputtering source is at low grazing angle to the sample's surface, while the detector and the primary electron source are perpendicular to the sample's surface, Figure 6.4 (B). Consequently, shaded regions which are highly enriched with Na, S, K, and Si will persist with sputtering.

Another measure of the elemental stratification within the submicron particle is provided by comparing the intensities from the low energy LMM Auger electron emission (~100 ev) and the high energy KLL Auger electron emission (~1000 ev) for each element (Kane and Larraby, 1974; King,
<table>
<thead>
<tr>
<th>species</th>
<th>surface conc. (wt%)</th>
<th>sputter 1 minute (wt%)</th>
<th>sputter 3 minute (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>11.8</td>
<td>6.0</td>
<td>4.6</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>5.6</td>
<td>3.7</td>
<td>1.8</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>16.4</td>
<td>6.4</td>
<td>3.5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>14.9</td>
<td>13.3</td>
<td>13.8</td>
</tr>
<tr>
<td>CaO</td>
<td>12.3</td>
<td>11.3</td>
<td>11.7</td>
</tr>
<tr>
<td>MgO</td>
<td>29.3</td>
<td>49.1</td>
<td>53.1</td>
</tr>
<tr>
<td>FeO</td>
<td>3.9</td>
<td>6.5</td>
<td>7.8</td>
</tr>
</tbody>
</table>
FIGURE 6.4 - Sectioned particle showing the contribution from the outer surface (A) and the shaded regions from the ion sputtering gun which are in view of the detector (B).
The extent of attenuation of the Auger electrons moving through a solid will be highly dependent on their mean free path (or escape depth \( \lambda \)) as is shown in the relationship:

\[
I(x) = I(o) e^{-x/\lambda} \quad \text{Eq. 6.1}
\]

where \( I(x) \) is the intensity of Auger signal after having traversed through a solid of thickness \( x \), \( I(o) \) is the intensity of the original signal, and \( \lambda \) is the mean free path of the Auger electron. For electron energies above 100 eV, the escape depth of an Auger electron is proportional to the energy of that electron, Figure 6.5. Consequently, the ratio of the intensity of high energy to low energy Auger emission for a subsurface element, relative to the ratio obtained from a homogeneous bulk standard, will increase as the distance of the element from the surface increases. Therefore, a comparison of the intensity ratios for the elements in the submicron particles with those from homogeneous bulk standards provides a measure of the distribution of sulfur, magnesium, and silicon as a function of depth, Table 6.5. For sulfur the ratio is close to, but slightly greater than, the ratio from the homogeneous bulk sample. The observed presence of identified surface-adsorbed carbon (as \( \text{CO}_2 \) and hydrocarbon), less than a monolayer in thickness on the fume surface, will lead to slight attenuation of sulfur's low energy Auger emission. Consequently, the results suggest that sulfur is in the outer surface layer of the submicron particle. For
Figure 6.5 - Escape depth of Auger electron verses electron energy
<table>
<thead>
<tr>
<th>element</th>
<th>electron energy</th>
<th>~ λA°</th>
<th>fume ratio standard ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>120</td>
<td>4</td>
<td>1.5</td>
</tr>
<tr>
<td>S</td>
<td>1834</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>76</td>
<td>4</td>
<td>10.4</td>
</tr>
<tr>
<td>Si</td>
<td>1606</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>35</td>
<td>6</td>
<td>54</td>
</tr>
<tr>
<td>Mg</td>
<td>1190</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>
magnesium, the ratio greatly exceeds that ratio from the homogeneous standard. The magnitude of the sample's intensity ratio, a result of extreme attenuation of magnesium's low energy Auger emission by the outer surface layer, suggests that magnesium is in the core of the particle. The extent of attenuation of the low energy emission for silicon indicates that this element lies between the outer surface layer enriched in elements such as sulfur and the particle's core enriched in elements such as magnesium.

The above data is only semi-quantitative due in part to the complexities derived from the differing degrees of attenuation by the Auger electrons emitted from different elements and also due to the averaging of emissions from different chords in the spherical particles. The results in Table 6.3 suggest that silicon is highly enriched in the surface layers, whereas the results in Table 6.5 suggest silicon is in an intermediate layer. The apparent anomaly can be explained by comparing the mean free path of silicon KLL Auger electron (~25 angstroms) to the mean free path of sulfur KLL Auger electron (~4 angstroms). The adsorbed carbon contamination present on the outer surface of the sample will probably attenuate the sulfur signal by a greater extent than the attenuation of the silicon signal by the outer surface layers. Therefore, Auger analysis of the outer surface yields an apparently high silicon concentration. Auger spectroscopy for analysis of the elemental stratification
within individual particles can be justified even though the particles are much smaller than the analysis area, since inter particle homogeneity has been established by STEM analysis.

6.4 CHEMICAL STATE ANALYSIS

Accurate chemical state identification by ESCA was determined for magnesium, iron, silicon, sulfur, sodium, and calcium. In general, identification of the oxidation state can be easily determined since measurable differences in the binding energy (> 1.0 eV) exist for the various oxidation states. On the other hand, differentiation between the various compounds is limited, since the difference in the resulting chemical shift may be small (< 1.0 eV). However, a large number of compounds can be readily eliminated because of the detailed knowledge about the chemistry of the submicron particle.

The extent of static charging for the fume sample was determined by comparing the observed binding energy for carbon Cls line (i.e., 287.3 eV) with the referenced binding energy (Wagner et. al., 1979) for adventitious carbon Cls line (i.e., 284.6 eV), Figure 6.6. The 2.7 eV shift in the observed binding energy for adventitious carbon from its reference binding energy is due to static charging of the insulating fume sample. Therefore, in order to correct this shifting, all observed binding energies will be adjusted by
Charge Shift of 2.7 eV

A - Measured carbon peak (287.3 eV)
B - Reference C 1s line (284.6 eV)

Figure 6.6 - ESCA high resolution scan of carbon C 1s line for fume sample
Figure 6.7 shows the high resolution scan for magnesium Mg2p line. A comparison of the observed binding energy for magnesium (49.1 eV) with the reference binding energy (Castleton, 1981) for magnesium metal (47.2 eV) and magnesium oxide (49.4 eV) suggest that the magnesium in the fume is present in its highest oxidation state. X-ray diffraction analysis of the fume confirms the presence of crystaline magnesium oxide, Figure 6.8. The slight shift in the diffraction lines is a result of impurities in the magnesium oxide crystals (Padro, 1981). Since the Auger analysis has indicated that the core of the submicron particles is composed of magnesium, calcium, and iron, the shift in the diffraction lines is probably due to dissolved iron and calcium. After correcting for static charging, the observed binding energy for magnesium, which has been independently shown to be present as magnesium oxide, is within 0.2 eV of the reference binding energy for magnesium oxide. This excellent agreement verifies the use of the carbon referencing technique to accurately determine the extent of static charge shifting for the insulating fume sample.

The high resolution scan for iron Fe2p3/2 line is present in Figure 6.9. A comparison of the observed binding energy for iron (711.1 eV) to the reference binding energy (Wagner et al., 1979) for iron (706.9 eV), FeO (709.5 eV), Fe2O3 (711.0 eV), and Fe3O4 (711.4 eV) suggests that the iron
Figure 6.7 - ESCA high resolution scan of magnesium Mg\textsubscript{2p} line for fume sample
Figure 6.8 - X-Ray diffraction lines for submicron particles
Figure 6.9 - ESCA high resolution scan of iron Fe$_{2p}$ line for fume sample
in the fume is present in its highest oxidation state as either Fe$_2$O$_3$ or Fe$_3$O$_4$.

Figure 6.10 shows the high resolution scan for silicon Si2p line. A comparison of the observed binding energy for silicon (101.7 eV) to the reference binding energy (Wagner, Gale, and Raymond, 1979) for silicon metal (99.0 eV), silicon dioxide (103.4 eV), and silicate (101.78 eV) suggests that the silicon in the fume is present in its highest oxidation state as a silicate. Identification by ESCA of the specific silicate compound is not possible. However, the chemical analysis also suggest that both alumina and some of the calcium are present in the sublayer of the particle with silicon. The concentration of aluminum in the submicron particles displays the same particle size dependence as silicon, Figure 6.2. This suggests that alumina heterogeneously condenses on the surface of the particles, thereby placing aluminum at or near the surface of the submicron particle. Auger analysis suggests that some of the calcium is near the surface of the particle.

The high resolution scan for sulfur S2p line is presented in Figure 6.11. A comparison of the observed binding energy for sulfur (168.8 eV) to the reference binding energy (Wagner et al., 1979) for sulfate ion (S$^{\text{4}^-}$ = 168.6 eV), sulfite ion (S$^{\text{3}^-}$ = 166.3 eV), elemental sulfur (S$^0$ ~ 163.9 eV) and sulfide ion (S$^2$ = 161.4 eV) establishes that sulfur is present in its highest oxidation state as a sulfate.
Figure 6.10 - ESCA high resolution scan of silicon Si$^{2p}$ line for fume sample
Figure 6.10 - ESCA high resolution scan of sulfur S\textsubscript{2p} line for fume sample
Auger analysis shows that sulfur is highly enriched in the outer surface of the particle. From the chemical characterization of the submicron particle the bulk of the sulfur will be present either as sodium sulfate (168.6 eV) and/or calcium sulfate (169.3 eV). The slight chemical shift in sulfur S2p line, due to the cation of calcium versus sodium, is not significant enough to permit differentiation between the two compounds.

Figure 6.12 shows the high resolution scan for sodium Na\textsubscript{1s} line. The photoelectron chemical shift is small, less than 2 ev, for the oxidation states of sodium. However, differentiation between the binding energy for some plausible sodium compounds is possible when a high resolution can be obtained with good statistics (i.e., narrow peak width). A comparison of the observed binding energy for sodium (1071.4 eV) to the reference binding energy (Wagner et. al., 1979) of Na\textsubscript{2}O (1072.5 eV), sodium chloride (1071.5 eV), and sodium sulfate (1071.3 eV) suggests that the sodium in the fume is present as either the chloride or the sulfate. The molar ratio of sulfur to sodium in the fume is 1:2, while the molar ratio of chlorine to sodium is less than 0.1:1. The proper stoichiometric molar ratio of sodium to sulfur and the insufficient chlorine in the fume tends to suggest that the bulk of the sodium is present as sodium sulfate.

Figure 6.13 presents the high resolution scan for calcium Ca\textsubscript{2p3/2} line. A comparison of the observed binding
Figure 6.10 - ESCA high resolution scan of sodium Na\textsubscript{1s} line for fume sample
Figure 6.13 - ESCA high resolution scan of calcium Ca2p3/2 line for the fume
energy for calcium (347.1 eV) to the referenced binding energy (Castleton, 1981) for calcium oxide (347.4 eV) and calcium sulfate (348.7 eV), suggests that calcium is present as calcium oxide.

The multiple analytical tools used in this investigation have lead to the development of a coherent story about the elemental stratification of the submicron particle. The core of the particle is composed of magnesium, calcium, and iron where their concentrations show no dependence on particle size. Furthermore, the x-ray analysis suggests the presence of dissolved impurities in the magnesium oxide crystals. The outer surface is composed of the volatile constituents whose concentration display a particle size dependence with the other trace species. Chemical state analysis shows that two of the surface enriched elements, sodium and sulfur, are present as sodium sulfate. The subsurface layer between these two strata is composed mostly of silicon whose concentration also displays a particle size dependence. Chemical state analysis demonstrates that silicon is present as a silicate of alumina and/or calcium. Both alumina, whose concentration displays a particle size dependence, and calcium, which has been shown by Auger analysis to be present near the surface as well as in the core of the particle, coexist in the subsurface layer with silicon.
CHAPTER SEVEN DISCUSSION

The examination of the bulk characterizatics of the submicron particles in chapter five has provided information about the amount, size, and bulk composition of these particles which have been shown to be dependent on both the combustion environment and the vaporization characteristics of the mineral matter. The detailed chemical characterization of the individual submicron particles in chapter six has provided specific information about the size dependence of composition for particles in the submicron range and on the elemental stratification within these particles. The information about the physico-chemical characteristics of the submicron particles presented in chapter five and six has provided some insight on the evolution of the submicron particles subsequent to their initial formation. The focus of this section will be to examine the hypotheses about the formation and subsequent growth of the submicron particles that can be inferred from the physico-chemical characteristics of the submicron particles. The discussion will pertain most closely to the conditions corresponding to the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen.
7.1 NUCLEATION

In the absence of a condensed phase, one or more of the vaporized inorganic elements should supersaturate, thereby, providing the necessary driving force for the onset of homogeneous nucleation. The free surface made available with the formation of the stable clusters (i.e., precursors of the submicron particles) can be expected to alleviate the supersaturation of the other inorganic vapors as a result of heterogeneous condensation (McNellan et. al., 1981; Martinez-Sanchez et. al., 1978). The elemental stratification of the submicron particles is believed to have provided a chronological signature of the condensation sequence for the various inorganic vapors. The elements present in the core of the submicron particles are believed to be responsible for the formation of the initial condensed phase by homogeneous nucleation, while those elements which form the outer layers of the submicron particles are believed to have condensed much later. The factors responsible for the initial formation of the submicron particles should be evident by examining the phenomena involving the vaporization and subsequent condensation of magnesium, which not only presides in the core of the submicron particle, but also accounts for over sixty percent of the submicron particle by weight.

The vaporization of the mineral matter has been
examined in a complimentary study by Richard Quann (1982). In the case of Montana lignite, the vaporization of magnesium was determined to be externally diffusion-limited. The experimentally observed high rate of vaporization for magnesium could not be explained by the direct vaporization of magnesium oxide into the gas phase. This was evident from the fact that the partial pressure of magnesium at the surface of the char particle calculated from the experimental vaporization data was found to exceed the equilibrium vapor pressure for magnesium oxide by several orders of magnitude (Quann, 1982). For the range of combustion conditions examined in this study (i.e., particle combustion temperatures > 2000 K), the rate of char oxidation will be externally diffusion-limited (Smith, 1978; Field et. al., 1967). Consequently, a locally reducing atmosphere will exist within the burning char particle, since oxygen penetration into the porous structure of the char particle will be minimal due to the high oxidation rate at the char surface. The NASA sp-273 equilibrium program can be used to calculate the equilibrium vapor pressure for the stable magnesium compounds in the presence of H, C, S, N, and O₂ over a wide range of fuel equivalence ratios. The results are presented in Figure 7.1 where for simplicity only CO₂, O₂, MgO(v), and Mg(v) are shown. The equilibrium vapor pressure for Mg(v) increases sharply as the conditions are changed from fuel lean to fuel rich, while the vapor pressure of magnesium oxide remains fairly constant up to a fuel equivalence ratio of 2.5. For
Figure 7.1 - Equilibrium vapor pressure for Magnesium for various fuel equivalence ratios

\[ \log_{10} (\text{EQUILIBRIUM VAPOR PRESSURE ATM}) \]

\[ \text{EQUIVALENCE RATIO} \]

TEMP = 2080 K

- Mg
- CO₂
- MgO
- O₂
the condition anticipated within the burning char particle (i.e., fuel equivalence ratio > 1) the metal is the dominate vapor species for magnesium which is shown to exceed the vapor pressure of the oxide by several orders of magnitude. The experimentally observed high rate of vaporization for magnesium can be explained by the chemical reduction of magnesium oxide in the condensed phase to the more volatile metal vapor.

The dramatic change in the environment as magnesium metal vapors diffuses from the locally reducing environment within the burning char particle out into the oxidizing atmosphere surrounding the char particle should account for the supersaturation of magnesium vapor. A scenario for the vaporization and subsequent condensation of magnesium is presented in Figure 7.2. In the locally reducing atmosphere within the char particle the vaporization of magnesium oxide will occur by chemical reduction to form the more volatile metal vapor. The metal vapor will be transported to the surface of the char particle. Once at the surface the metal vapors will diffuse away from the burning char particle into the surrounding oxidizing environment, where the metal vapors will reoxidize. Upon reoxidization, the magnesium oxide vapors will be supersaturated, thus providing the necessary driving force for homogeneous nucleation. The decrease in temperature away from the burning char particle can only accentuate the tendency for the supersaturation of the magnesium vapors.
diffusion of Mg vapors from char

oxidation

\[ \text{Mg}(v) + \text{O}_2 \rightarrow \text{MgO}(v) + \text{O} \]

---

\[ \text{MgO}(s) + \text{CO} \rightarrow \text{Mg}(v) + \text{CO}_2 \]

formation of condensed phase

REDUCING ATMOSPHERE

\[ P_{\text{eq. Mg}} \gg P_{\text{eq. MgO}} \]

CHAR PARTICLE SURFACE

OXIDIZING ATMOSPHERE

\[ P_{\text{magnesium}} \gg P_{\text{eq. MgO}} \]

Figure 7.2 - Schematic diagram of magnesium vaporization and recondensation during char combustion
upon reoxidation. The point at which magnesium supersaturates will be dependent on the rate of oxidation and the oxygen potential, the subsequent partial pressure of magnesium oxide, and the gas temperature at various distances from the char particle.

A steady state one dimensional model was developed in order to examine in detail the phenomena involving the homogeneous nucleation of magnesium oxide around the char particle. The model estimates the temperature, oxygen partial pressure, magnesium metal partial pressure, and magnesium oxide partial pressure from the governing differential equation as a function of distance from the char particle. The major assumption about the present model is that a barrier exist for both the oxidation of the metal and the initial formation of the condense phase despite the large potentials that may exist.

From two color optical pyrometry the particle combustion temperature has been shown to overshoots the bulk gas temperature (Timothy, 1982). Consequently, a temperature gradient will exist between the char particle's surface and the bulk gas phase. The temperature at various distances from the char particle was derived for spherical coordinates from Fourier's first law of heat conduction,

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) = 0 \]

Eq. 7.1
where the particle temperature was determined from two color pyrometry. The magnesium partial pressure is low enough that the heat released upon oxidation and condensation should not perturb the temperature profile in the thermal boundary layer. The heat effect from the oxidation of CO in the gas stream has not been considered, since the rate of oxidation of CO is extremely slow.

For externally diffusion-limited combustion, an oxygen gradient will exist between the bulk gas phase and the char particle's surface. The oxygen partial pressure at various distances from the char particle was derived for spherical coordinates from Fick's first law,

\[
\frac{1}{r^2} \frac{d}{dr} \left( r^2 D_{AB} \frac{dn_{O2}}{dr} \right) = 0 \quad \text{Eq. 7.2}
\]

where the oxygen partial pressure at the surface of the char particle was calculated from the char oxidation kinetics (Field et al., 1967). The consumption of oxygen in the boundary layer by the oxidation at the metal vapors and carbon monoxide have not been considered.

The partial pressure of magnesium at various distance from the char surface was governed by the differential equation for spherical coordinates
where the partial pressure of magnesium metal at the surface of the char particle was calculated from experimental vaporization data (Quann, 1982). The reaction term on the right hand side of equation 7.3 accounts for the consumption of magnesium metal by oxidation. The modeling of the homogeneous gas phase oxidation of magnesium will entail establishing the rate coefficient for the governing bimolecular reaction

\[ \text{Mg}(v) + \text{O}_2 \rightarrow \text{MgO}(v) + \text{O} \quad \text{Eq. 7.4} \]

as proposed by Markstien (1963). The low pressure, low temperature studies concluded that the bimolecular homogeneous reaction will account for initial formation of magnesium oxide vapors which, upon supersaturation, will homogeneously nucleate to form the initial particles. For the atmospheric high temperature environment of combustion, the estimated rate coefficient from collision theory was used to model the bimolecular oxidation of magnesium metal vapors (Laider, 1965)

\[ K = A T^n e^{-E/RT} \quad \text{Eq. 7.5} \]
The partial pressure of magnesium oxide at various distance from the char surface was governed by the differential equation in spherical coordinates,

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 D_{AB} \frac{dn_{MgO}}{dr} \right) = R_{rxn} + R_{nucl} + R_{het} \quad \text{Eq. 7.6} \]

\[ R_{rxn} = k n_{Mg} n_{O_2} \]
\[ R_{nucl} \sim I \]
\[ R_{het} \sim F'(d) \]

where the reaction terms on the right hand side of equation 7.6 accounts for; the continual addition of magnesium oxide vapor by oxidation of the metal vapor, \( R_{rxn} \); the consumption of magnesium oxide vapors by homogeneous nucleation, \( R_{nucl} \); and the consumption of magnesium vapors by heterogeneous condensation on the stable nuclei of magnesium oxide.

The rate of homogeneous nucleation of a spherical liquid droplet from unary vapors can be calculated from the classical theory of nucleation of volmer and weber and Becker and Doering (Hirth and Pound, 1963). The rate of nucleation, \( I \) (nuclie/cc s), is given by

\[ I = \frac{2 \sigma_c p_i^2}{(2 \pi m)^{1/2} (kT)^2} \left( \frac{1}{V_m} \right) \exp \left\{ - \frac{16 \pi \sigma^3}{3 k T \Delta G_v^2} \right\} \quad \text{Eq. 7.7} \]

\[ A = 4.44 \times 10^{18} \text{ m}^3/\text{mole sec} \]
\[ n = 1/2 \]
\[ E = 1.28 \times 10^5 \text{ joules/mole} \]
\[ \Delta G_v = \frac{kT}{V_m} \ln \left( \frac{P_i}{P_{eq,i}} \right) \]

where \( \alpha_c \) is the condensation coefficient (the fraction of molecules that collide with an embryo and stick), \( P_i \) and \( P_{eq,i} \) are the partial and equilibrium pressure of the vapor species \( i \), \( \sigma \) is the surface tension of liquid \( i \), \( V_m \) is the molecular volume, \( m \) is the mass of molecule \( i \), \( k \) is boltzman constant, and \( \Delta G_v \) is the change in Gibbs' free energy for droplet formation per unit volume. The development of the classical nucleation theory is based on the considerations imposed by both thermodynamics (i.e., stability) and kinetics (i.e., probability). In other words, the rate of nucleation is governed by the net number of clusters per unit time which grow larger than the critical cluster size. The critical cluster is a cluster of size such that its rate of growth is equal to its rate of decay. Any cluster which fluctuates to a size larger than the critical size will probably grow to macroscopic size while clusters smaller that the critical size will most likely shrink back to the monomer. The critical cluster size is determined from the relation,

\[ r^* = \frac{2 \sigma V_m}{kT \ln (P_i/P_{eq,i})} \]

Eq. 7.8

where the addition of one monimor leads to the formation of a stable cluster.
The rate of heterogeneous condensation of the condensable vapor molecules on the newly formed stable cluster of magnesium oxide whose size is much smaller than the mean free path of the gas molecule will be controlled by the frequency with which the vapor molecules collide with the particles. The rate of deposition per particle of size \( dp \) is derived from the kinetic theory of gases (Friedlander, 1977)

\[
F'_{i}(d) = \frac{\pi d_p^2 \alpha_c (P_i - P_{eq,i})}{(2 \pi m k T)^{1/2}} 
\]

where \( \alpha_c \) is the condensation coefficient and is assumed to have a value of be unity. The rate of heterogeneous condensation for the condensable vapors obtained from the rate of deposition per particle and the number density of stable nuclei of magnesium oxide. The overall rate of heterogeneous condensation will be highly dependent on the number density and size distribution of the particles. The details of the growth process of the particles by coagulation will be dealt with in detail in section 7.2. However, in assuming nearly monodispersed particle size, a simple solution to the kinetic equation for brownian coagulation can be used to approximate the number density and average particle size of the stable nuclei of magnesium oxide. The decay in the total number of particles with time is approximated from the rate expressions

\[
\frac{dN}{dr} = -\frac{1}{2} K N^2 
\]

Eq. 7.10
where the collision frequency factor, $K$, is given by

$$K = \frac{8 k T}{\mu} \quad \text{Eq. 7.11}$$

The average particle size can be approximated from the volume fraction and the total number of particles.

The model's prediction for the condensation of magnesium are presented in Figure 7.3 for the conditions corresponding to the combustion of Montana lignite in twenty percent oxygen in nitrogen. The supersaturation of magnesium is predicted to occur within the thermal boundary layer of the char particle due to the relatively high rate for the homogeneous oxidation of magnesium. The model predicts a very sharp rise in the nucleation rate as supersaturation increases. This position is relatively insensitive to uncertainties in the assumed values for the oxidation rate constant and surface tension (Smithells, 1965), and the estimate of the partial pressure for magnesium oxide and oxygen at the char particle's surface. Since the onset of nucleation is very sensitive to temperature, changes in the values assumed for the above parameters will result in only a slight displacement of the position of nucleation because of the steep temperature gradient near the char particle's surface. The duration of the nucleation is attributed to the
Figure 7.3 - Model prediction for the supersaturation and condensation of magnesium
continual addition of monomer by homogeneous gas phase oxidation of magnesium metal vapor. Since the transient time for establishing the steady state gas and temperature profiles around the char particle is extremely short and the fact that the characteristic times for oxidation and nucleation are over two orders of magnitude shorter than the time for char burnout, magnesium can be inferred to homogeneously nucleate very early on during the combustion process where the temperature is relatively high. Experimental observations indicate that the submicron particles form very early on during the combustion process, as shown in the time resolve study in Figure 5.17.

The present model predict that the submicron particles form very early on during the combustion process which is supported by experimental observation. This has been shown to be a direct consequence of the mechanism of vaporization where the refractory oxides are chemically reduced to form the more volatile metal vapor, and the sharp temperature gradient surrounding the char particle. As the metal vapors diffuse into the oxidizing environment, the metal vapors reoxides forming supersaturated oxide vapors which account for the early formation of the submicron particles. Before examining the sequence of condensation for the other inorganic species relative to magnesium, the growth process of the submicron particles will be examined more closely, since the presence of these particles may influence the condensa-
tion process for the other inorganic vapors.

7.2 COAGULATION

The formation of the inorganic submicron particles have been shown to result from the homogeneous nucleation of the supersaturated vapors of magnesium oxide in the boundary layer of the burning char particle. The classical nucleation theory predicts the formation of an extremely large number of stable nuclei with critical radii of six angstroms. The high particle mobility of these extremely small particles will result in a high frequency of particle-particle collisions. The colliding particles which stick upon contact should coalesce to form single spherical particles. The term "coagulation" describes the growth process for aerosol systems where the random particle-particle collision account for the reduction in the total number of particles and coalescence accounts for the increase in the average size of the primary particles. From the physical characterization of the submicron particles in chapter five, the size of the primary particles was found to be dependent on both the residence time and the total mass in the submicron mode.

By convention, the rate of coagulation is designated by the collision frequency of the particles where the subsequent coalescence of the colliding particles is assumed to occur instantaneously. The kinetics governing the collision frequency of the particles as a result of brownian motion in
a uniform flow field (Smoluchowski, 1917) can be used to determine the decay in the total number of particles with time

$$\frac{dN}{dt} = -\frac{1}{2} \int_0^\infty \int_0^\infty B(v,u,t) n(v,t) n(u,t) \, dv \, du$$

Eq. 7.12

where $n(u,t)$ is the particle volume distribution function and $B(v,u)$ is the collision frequency between particles of volume $v$ and $u$ (Lai et. al., 1972). For particles much smaller than the mean free path of the gas molecules (i.e., free molecular regime), the collision frequency factor, $B(v,u)$, is derived from the kinetic theory of gases for collisions among molecules that behave as rigid elastic spheres (i.e., noninteracting spheres)

$$B(v,u) = a \left( \frac{3}{4\pi} \right)^{1/6} \left( \frac{6kT}{\rho} \right)^{1/2} \left( \frac{1}{v} + \frac{1}{u} \right)^{1/2} \left( v^{1/3} + u^{1/3} \right)^2$$

Eq. 7.13

where $k$ is boltzman constant, $T$ is the absolute temperature, $\rho$ is the particle density, and $a$ is the sticking coefficient which is assumed to have a value of unity (Hidy and Brock, 1970). For the case of noninteracting spheres, interaction forces such as electronic or intermolecular are neglected. In examining the free molecular coagulation kinetics for molten lead aerosols, dispersion forces were found to account for the enhancement in the collision frequency of the particles (i.e., $G=2$) (Graham and Homer, 1972). The origin of the dispersion forces resulted from a theoreti-
The total number of particles per unit volume, \( N_\infty \), and the volume fraction of the dispersed phase, \( V \), can be expressed in the form:

\[
N_\infty(t) = \int_0^\infty n(v,t) \, dv \quad \text{Eq. 7.14}
\]

\[
V = \int_0^\infty v \, n(v,t) \, dv \quad \text{Eq. 7.15}
\]

For pure coagulation in the absence of condensation, evaporation, or particle loss by settling or diffusion, the volume fraction, \( V \), will be invariant with respect to time.

The partial integro-differential equation governing particle coagulation can be solved numerically, however the calculations become extremely cumbersome due to the increase in particle inventory with time. However, with the discovery that the evolving particle size distribution of an aerosol whose growth is governed by coagulation approaches an asymptotic form with time (i.e., self-preserving), a class of analytical solutions have been developed based on the use of a similarity transformation for the particle size distribution (Swift and Friedlander, 1964; Friedlander and Wang, 1966). The unique feature of the self-preserving particle size distribution function is that once the particle size distribution conforms to the self-preserving distribution, the normalized distribution will be invariant with time and
independent of the individual peculiarity of the initial particle size distribution. The similarity transformation for the particle size distribution, \( n(v,t) \), is based on the assumption that the fraction of the particles in a given size range is a function only of particle volume, \( v \), normalized by the mean particle volume, \( \bar{v} \),

\[
\frac{n(v,t)}{\bar{v}} = \frac{N_0^2(t)}{\bar{v}} \psi(\eta) \quad \text{Eq. 7.16}
\]

where

\[
\eta = \frac{v}{\bar{v}} = \frac{N_0(t)}{\bar{v}} \quad v
\]

Since the collision frequency factor, \( B(u,v) \), is a homogeneous function, the similarity transformation of the particle size distribution will reduce the kinetic equation governing the decay of the total number of particles, equation 7.12, to an ordinary integro-differential equation

\[
\frac{dN}{dt} = -\frac{6}{2} \left( \frac{3}{\pi 4} \right)^{1/6} \left( \frac{6kT}{\rho} \right)^{1/2} N^{1/6} \quad \text{Eq. 7.17}
\]

where \( \delta \) is the dimensionless collision integral for the self-preserving distribution, \( \psi(\eta) \), and is found to be 6.67 by numerical analysis (Lai et al., 1972). The analytical solution to equation 7.17 yields a simple expression for the time dependence of the number of particles in the system.
\[
N(t) = \left( \frac{1}{(K_{\text{theory}} V^{1/6} t + \frac{1}{N_0} 5/6)} \right)^{6/5} \\
\text{Eq. 7.18}
\]

where

\[
K_{\text{theory}} = \frac{5}{12} \left( \frac{3}{4\pi} \right)^{1/6} \left( \frac{6kT}{p} \right)^{1/2} G
\]

For coagulation times on the order of one millisecond, \((K_{\text{theory}} V^{1/6} t)\) will be much larger than \((1/N_0)^{5/6}\).

Therefore, equation 7.18 can be further simplified

\[
N(t) = (K_{\text{theory}} V^{1/6} t)^{-6/5} \quad \text{Eq. 7.19}
\]

where the predicted number density, \(N(t)\), will be independent of the initial particle number density for coagulation times greater than several milliseconds. From the mean particle volume identity, \(v = V/N\), the time dependence of the volume average particle diameter of the coagulating particles can be obtained:

\[
d_p = \left( \frac{6}{\pi} \right)^{1/3} (K_{\text{theory}} V t)^{2/5} \quad \text{Eq. 7.20}
\]

In order to examine the volume fraction and time dependence for the growth of the inorganic submicron particles with that predicted by coagulation kinetics (i.e., equation 7.20), the distribution of the submicron particles must be self-preserving. In Figure 7.4, the particle size distribu-
Figure 7.4 - Primary particle size distribution for the fume with the self-preserving distribution.
tion of the primary submicron particles produced from the combustion of Montana lignite 45/53 um in 15, 20, and 40 percent oxygen are fairly well represented by the self-perserving size distribution. The calculated transient time for the transformation of the initial distribution for the submicron particles to self-preserving is on the order of several milliseconds (Hyde and Lilly, 1965).

In order to examine the time dependence for the growth of the primary submicron particles, time resolve measurements were conducted where samples of the submicron particles were collected at various distances from the point of coal injection. The time resolve measurements of the experimentally determined mean particle diameters for the primary submicron particles produced from the combustion of Montana lignite 45/53 um at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen are compared with those predicted from coagulation theory (i.e., equation 7.20) in Figure 7.5. The predicted curve for the mean particle diameters were generated using the appropriate value for the volume fraction and elapsed time where the formation of the initial submicron particles was assumed to occur at the initiation of char combustion. The volume fraction is obtained from the measured value of the fractional vaporization for the metal oxides, $\phi$, assuming that the fume particles remain within the core along the furnace axis in which the coal particles are visually observed to burn (i.e., core
Figure 7.5 - Experimental and predicted growth of the primary submicron particles
radius of 0.62 centimeters). This is reasonable because on
the time scale of the experiments, particle transport by
diffusion can be neglected. The experimental mean diameter
of the primary particle is determined by the automated image
analyser from electron micrographs as previously described.

In examining the growth curve in Figure 7.5, coagu-
lation theory provides an excellent representation of the
changes in the primary particle size with time for the early
growth period between 3.81 to 6.35 centimeter. The primary
particle size is observed to increase rapidly as the large
number of small nuclei collide and coalesce. Coagulation
brings about the decrease in particle number density from
$2.76 \times 10^{11}$ particles/cc at 3.81 centimeters to $6.24 \times 10^{10}$
particles/cc at 6.35 centimeters while the volume mean
diameters of the particle increases from 34 angstroms to 139
angstroms, respectively. During char combustion, new
material is continuously added to the vapor phase by further
vaporization. Originally, it had been assumed that no
subsequent nucleation would occur after the initial forma-
tion of the submicron particles, because the concentration
of the inorganic vapor continually released during combus-
tion was anticipated to remain close to the saturation vapor
pressure as a consequence of heterogeneous condensation on
the surface of the particles produced by the initial nuclea-
tion wave (McNellan et. al., 1981; Martinez-Sanchez et. al.,
1978). However, the thermophoretic forces resulting from
the steep temperature gradient surrounding the burning char particle will rapidly drive the particles away from the char's surface. Consequently, the steady state one dimensional model suggests that magnesium will continuously nucleate close to the char particle as long as vaporization persists. Since magnesium is the dominate species which makes up the submicron particles, the contribution from the other inorganic vapors condensing during char combustion will be minimal. However, the continuous addition of new particles should be rapidly accommodated, since a much higher rate of coagulation will exist between the newly formed particles with their high mobility and the older particles with their larger cross sectional area (Friedlander, 1977). The success of the coagulation model for predicting the growth of the submicron particles in the char combustion zone further supports the assumption that the addition of new particles will be rapidly accommodated.

In examining the growth curve in Figure 7.5, the growth of the primary particles ceases shortly after the sampling point at 8.9 centimeters from the point of coal injection. The apparent brake between theory and that observed experimentally may be explained by a decreased in the coalescence rate after char burnout as the gas temperature drops back down to the furnace gas temperature of 1700 K and as the particle diameter approaches 160 angstroms. Since the particles during the early growth period have been
proposed to be composed of magnesium, iron, and calcium and the fact that these particles should be solid below 1800 K, the coalescence rate for these particles at the furnace gas temperature of 1700 K will be governed by solid state diffusion. The difference in free energy or chemical potential between the neck area and the surface of the two particles provide a driving force for solid state diffusion where the transfer of material along the grain boundary between the two particles will be responsible for the decrease in the distance between the particles' centers (i.e., coalescence). The time for coalescence, governed by solid state diffusion for two solid particles with identical diameters may be estimated from the relationship

\[ t = \left( \frac{\Delta L}{L_0} \right) \frac{(2 \kappa T)^{6/5}}{(20 a^3 D^*)^{5/2}} \]  

Eq. 7.21

where \( \Delta L/L_0 \) is the fractional shrinkage of the coalescing particles, \( a^3 \) is atomic volume of diffusing vacancy, and \( D^* \) is the self diffusion coefficient (Kingery, 1965). From inspection the coalescence time will be governed by the particle size, composition, and temperature. A solid phase diffusion coefficient for crystalline magnesium oxide was selected to derive estimates of the coalescence time for the primary submicron particles during the early stages of growth where only magnesium, calcium, and iron have been proposed to condensed. Figure 7.6 shows the estimated
Figure 7.6 - Predicted coalescence time for solid crystalline magnesium oxide particles
coalescence time as a function of both temperature and particle size. The local gas temperature surrounding the burning char particle will exceed the main gas furnace temperature due to the liberation of heat during combustion. Consequently, both the decrease in temperature on completion of combustion and the increase in particle diameter both contribute to the decrease of the coalescence rate. The primary particle diameter is in the range of 120 to 160 angstroms when both these factors become important. Beyond this point further coagulation leads to the formation of agglomerated particles where the discrete size of the colliding particles is conserved. The projected area of the agglomerated particle at sampling position of 20 centimeters from the point of coal injection is in very good agreement with coagulation theory. The fact that the coalescences of these particles cease at relatively high temperatures (i.e., 1700 K) is consistent with the hypothesis that the species Na, S, and, K heterogeneously condense well after the particles have solidified and only upon cooling of the combustion products since these impurities would tend to increase the coalescence rate (Kingery, 1965).

Coagulation theory predicts that the volume average particles diameter for equivalent coagulation time should vary as $V^{2/5}$, or as $\phi^{2/5}$ since the volume fraction, $V$, is proportional to the fractional vaporization, $\phi$. The particle size dependence for the primary submicron particles
are shown to be well governed in Figure 7.7 by the fractional vaporization to the \(2/5\)th power. The value of \(\phi\) from 0.002 to 0.15 were generated from the combustion of Montana lignite (38/45 um) in oxygen concentration varying from ten percent to seventy five percent in nitrogen at 1700 K. The major assumption in presenting the mean particle diameter verses the fractional vaporization of the metal oxides to the two fifths power is that the coagulation time for the primary particles for the range of conditions examined are equivalent. In examining the growth curve for the primary submicron particles produced from the combustion of Montana lignite in seventy five percent oxygen in nitrogen, Figure 7.8, the duration for the coalescence for the submicron particles produced in twenty percent and seventy five percent oxygen is relatively equivalent despite the difference in burning time for the two conditions. As anticipated, coagulation theory is shown to provide a good representation of the change in the the primary particle size with time for the early growth period. However, the growth of the primary submicron particle ceases shortly after the sampling point of 8.9 centimeters from the point of coal injection. The coalescence of much larger particle sizes (i.e., 400 angstroms) tends to suggest that the local gas temperature is much higher than the main gas temperature of 1700 K during and immediately following char combustion. The relationship between mean particle radius and fractional vaporization for similar growth times is further conforma-
Figure 7.7 - Variation of mean diameter of primary submicron particle with degree of vaporization of the ash
Figure 7.8 - Experimental and predicted growth of the primary submicron particles
tion that particle growth is well governed by coagulation kinetics.

7.3 HETEROGENEOUS CONDENSATION

The formation of the inorganic submicron particles have been shown to result from the homogeneous nucleation of the supersaturated vapors of magnesium oxide in the boundary layer of the burning char particle. If the total area of the stable nuclei of magnesium oxide is sufficiently high, those species which saturate outside the boundary layer of the char particle are anticipated to condense heterogeneously on the surface of these particles, thereby, decreasing the driving force for homogeneous nucleation of those condensable vapors.

The mechanism of mass transfer between particles and the gas phase will depend on the particle size relative to the mean free path of the gas molecules. This relationship between particle size and mean free path of the gas molecules is defined by the knudsen number, \( \text{Kn} = \frac{2 \lambda}{d_p} \).

For particles much larger than the mean free path of the gas molecules (i.e., continuum regime \( \text{Kn} \ll 1 \)), a concentration gradient of condensable gas molecules will exist around each particle. For continuum particle dynamics (\( \text{Kn} \ll 1 \)), the rate of diffusion-limited heterogeneous condensation is given by
where $F_i(d)$ is the flow of condensable gas molecules per unit time to the surface of a spherical particle of diameter $d_p$ (Friedlander, 1977). The number of molecules condensing on particles of size $d_p$ per unit mass of the particle can be expressed as

$$F_i(d) = \frac{2\pi d_p D (P_i - P_{eq,i})}{k T} \quad \text{Eq. 7.22}$$

and

$$\frac{F_i(d)}{\rho_p(\pi/6)d_p^3} \propto \frac{1}{d_p^2} \quad \text{Eq. 7.23}$$

Thus, for the continuum regime the concentration dependence of a species which condense heterogeneously will be inversely proportional to the particle diameter squared.

For particles much smaller than the mean free path of the gas molecules (i.e., free molecular regime, $Kn >> 1$), the rate of deposition of the condensing inorganic vapors on the particle's surface will be controlled by the frequency with which the vapor molecules collide with the particles. Therefore, the rate of deposition of the condensable inorganic vapors on the surface of those particles will occur by a random fashion in the absence of a concentration gradient. The rate of deposition per particle of size $d_p$ is derived from the kinetic theory of gases (Friedlander, 1977).
\[ F'_i(d) = \frac{c \pi d_p (P_i - P_{eq,i})}{(2 \pi m k T)^{1/2}} \]  

Eq. 7.24

where \( c \) is the condensation coefficient and is assumed to have a value of unity. The number of molecules condensing on a particle of size \( d_p \) per unit mass of particle can be expressed as

\[ \frac{F'_i(d)}{(\rho_p (\pi/6) d_p^3)} \propto \frac{1}{d_p} \]  

Eq. 7.25

Thus, for the free molecular regime the concentration dependence of a condensing species will be inversely proportional to the particle diameter.

In the transition regime between the continuum and free molecular regime (i.e., \( 10 > Kn > 1 \)), the rate of deposition of the condensable inorganic vapors is governed by the relationship proposed by Fuchs and Sutugin (1971).

\[ F_i(d) = \frac{2 \pi d_p D (P_i - P_{eq,i})}{k T} \left( \frac{1}{1 + Kn} \right) \]  

Eq. 7.26

In the limit of the continuum particle dynamics (i.e., \( Kn \ll 1 \)), equation 7.26 reduces to equation 7.22, while in the limit of the free molecular particle dynamics equation 7.26 will approach the form of equation 7.24 if the diffusion
coefficient is given by $D = \frac{1}{3} C$ where the average velocity of the vapor molecules, $C$, is expressed as $(8kT/\pi m)^{1/2}$.

### 7.3.1 REFRACTORY OXIDES

The steady state one dimensional model presented in section 7.1 will be used to examine the condensation pathway (i.e., homogeneous verses heterogeneous) for the oxides of calcium, iron, and silicon in the presence of the stable nuclei of magnesium oxide.

In a manner analogous to magnesium, the vaporization of calcium, iron, and silicon is augmented by the chemical reduction of these refractory oxides to their more volatile suboxide (SiO) or metal (Ca and Fe) vapor due to the locally reducing environment within the char particle (Quann, 1982). As those vapors diffuse into the oxidizing environment surrounding the burning char particle, the vapors of those reduced species will reoxidize. The sequence of condensation for the refractory oxides of calcium, iron, and silicon will be highly dependent on the rate coefficient for their oxidation and their relative partial pressure. Subsequent to the formation of stable nuclei, one might anticipate an increase in the oxidation rate by heterogeneous oxidation of the metal or suboxide vapors by collision with the oxygen atom layer formed on the surface of the growing particles. The contribution of this mechanism to MgO formation is estimated to be two orders of magnitude smaller than that due to homo-
geneous oxidation, even when neglecting the low collision efficiency of magnesium atoms with the surface at high temperatures (Markstien, 1969; Glassman, 1959).

Silicon condenses late relative to magnesium, calcium, and iron because the silicon concentration is low and its rate of oxidation is slow. The silicon monoxide vapor pressure at the surface of the char particle is reduced to a level below the equilibrium value because of a diffusional resistance within the char particle. Such a diffusional limitation is not important for magnesium and calcium because magnesium and calcium are atomically dispersed in the original coal particle in contrast to silicon which is present in discrete mineral inclusions (Quann, 1982). The rate of oxidation of a monoxide such as SiO to SiO$_2$ is expected to be much slower than that for the oxidation of a metal to the monoxide; this statement is based on an analogy with aluminum for which it was found that the oxidation of aluminum by $O_2$ to AlO is two orders of magnitude faster than that of AlO to AlO$_2$ (Fontijn, 1976). The proximity of the saturation of calcium and iron to the surface of the burning char particle as determined from steady state model suggests that these species like magnesium condense shortly after the onset of char combustion. However, the model's prediction for the condensation of silicon in the presence of stable nuclei of magnesium oxide, Figure 7.9, suggest that the bulk of the silicon will condense heterogeneously only upon the comple-
Figure 7.9 - Profile of SiO and SiO$_2$ at various distances from char particle's surface
tion of char combustion where the local gas temperature drops back to the furnace temperature of 1700 K.

The proximity of the saturation of calcium and iron to the surface of the burning char particle suggest that these species like magnesium condense shortly after the onset of char combustion, while silicon is shown to saturate only as the local gas temperature drops back to the furnace temperature upon completion of the combustion of the char particles.

The submicron particles are small enough to exhibit free molecular behavior (i.e., $Kn \sim 100$). Consequently, the concentration dependence of those species which condense heterogeneously on the surface of the submicron particles is predicted to be inverse proportional to particle diameter, equation 7.25. Of the major refractory oxides examined only silicon displays a particle size dependence, section 6.3. From the STEM analysis of individual submicron particles, the concentration dependence for silicon is best correlated with inverse diameter, Figure 7.10 while the concentration of magnesium, calcium, and iron show no dependence on particle size. From the growth process of the submicron particles the relative uniform concentration for magnesium, calcium, and iron with particle size can be explained. During and shortly after the completion of the combustion of the char, the growth of the submicron particles have been shown to be well predicted by the classical coagulation theory where the
Figure 7.10 - Elemental concentration for primary particle by STEM verses inverse diameter

- △ - Mg x 0.2
- □ - Si x 10
- ○ - Ca
- □ - Fe x 0.5
colliding particles rapidly coalesce upon contact. However, as the local gas temperature drops back to the furnace temperature upon completion of the combustion of the char and as the primary particle size increases, the coalescence rate is shown to decrease sharply where further coagulation leads to the formation of aggregates. The condensation of magnesium, calcium and iron are predicted to account for the initial formation of the submicron particles where the growth of the particles from the critical cluster size of six angstroms to the final primary particle size of one hundred fifty angstroms will entail the coalescence of a large number (i.e., \( \sim 1.0 \times 10^4 \)) of various sized particles. Consequently, the interparticle concentration of those species which condense relatively early during the growth process should be relatively uniform as is observed for the case of magnesium, calcium, and iron. However, in the case of silicon, the predicted particle size dependence is preserved since silicon has been shown to condense heterogeneously after the coalescence of the primary particles has ceased. The late condensation of silicon relative to the other refractory oxides is further supported by Auger spectroscopy which has shown the bulk of the silicon to be present near the outer surface of the submicron particles while magnesium, calcium, and iron are shown to make up the core of the submicron particles, section 6.3.

7.3.2 VOLATILE AND TRACE SPECIES
The volatile and trace species are assumed to condense at much lower temperatures than the refractory oxides of calcium, magnesium, iron, and silicon either because they are present in dilute quantities or they have much higher vapor pressures than the refractory oxides. Whether these species condense heterogeneously or homogeneously will be highly dependent on the area of the residual and primary submicron particles available for heterogeneous condensation and the rate at which the combustion products are cooled.

The method employed for determining whether homogeneous nucleation of the volatile and trace species can occur in the presence of the pre-existing particles will be determined by establishing whether or not the criteria for homogeneous nucleation has been exceeded. Classically, the criteria for homogeneous nucleation has been defined by that condition at which the nucleation rate exceeds one nuclei per cubic centimeter per second (Hirth and Pound, 1963). From classical nucleation theory, section 7.1, the critical supersaturation partial pressure required for the onset of homogeneous nucleation (i.e., \( I = 1 \) nuclei/cc sec) can be calculated. As the combustion products are cooled the volatile and trace species will eventually saturate. As the gases are cooled further, the partial pressure of species \( i \) will be determined by calculating the amount of the condensable vapor that condenses heterogeneously on the the pre-existing particles over the short time increment at each temperature. The
amount of condensable vapor species remaining in the gas phase after each step will be used as the starting amount for the next time increment at the next temperature. If the partial pressure of species \( i \) exceeds its critical supersaturation partial pressure at any point during cooling, homogeneous nucleation in the classical sense is assumed to occur. The trace and volatile species are presumed to condense only as the gases are being cooled where the particle size distribution for the residual and submicron fly ash particles are well established. Therefore, the contribution from both the residual and submicron fly ash particles will be considered in the present model.

For diffusion-limited heterogeneous condensation, the amount of condensing volatiles will be determined from the flux integral:

\[
\int_0^\infty n(v) F_i(v) \, dv \quad \text{Eq. 7.27}
\]

For the residual ash particle mode, the particle size distribution function, \( n(v) \), is approximated numerically from the experimental data. Thus, the flux integral becomes

\[
\sum_{k=0}^{7} n_k F_i(d_k) \quad \text{Eq. 7.28}
\]

where \( n_k \) is the number density of particles in the size range
corresponding to stage $k$, and is given by $n_k = \phi_k V / v_k$. Here, $\phi_k$ is the fraction of the total ash appearing on stage $k$ and $v_k$ is the average particle volume for that stage (see Table 3.1) while $V$ is the total ash volume fraction (see section 7.2). In order to account for the non-continuum behavior of the smaller residual fly ash particles (stage 6 and 7), the molecular diffusion flux, $F_i(d_k)$, for the transition regime is substituted into equation 7.28. The required sum is therefore

$$\frac{12VD}{RT} \left( P_i - P_{eq,i} \right) \sum_{k=0}^{7} \frac{\phi_k}{d_k^2} f_{FS}(d_k) \quad \text{Eq. 7.29}$$

The submicron particles exhibit free molecular behavior (i.e., $kn > 10$) and obey the self-preserving size distribution function, $\psi(\eta)$, when $\eta = v/\bar{v}_f$ and $\bar{v}_f$ is the average submicron particle volume (Friedlander, 1977). In transforming the size distribution function, $n(v)$, of the submicron particles for self-preserving (see section 7.2) and substituting the molecular diffusion flux, $F_i'(d_p)$, from equation 7.24 to account for the free molecular behavior of the submicron particles, the flux integral becomes

$$\frac{12VD}{RT} \left( P_i - P_{eq,i} \right) \frac{\pi \phi}{0.65 \lambda d'_f} G \quad \text{Eq. 7.30}$$
where
\[ G = \int_{0}^{\infty} \eta^{2/3} \psi(\eta) \, d\eta \]

The 2/3-moment of \( \psi(\eta) \) represented by \( G \) has the value 0.90. Depending on the magnitude of the potential for condensation, \( (P_i - P_{eq,i}) \), the kelvin effect, which accounts for the elevated vapor pressure over extremely small particles due to their curvature, will preferentially reduces the potential for condensation to the smaller particles (i.e., diameter < 1000 angstroms). An expression for the vapor pressure, \( P_d \), over a drop of diameter \( d_p \) has been derived from thermodynamics (Friedlander, 1977)

\[ P_d = P_{eq} \exp \left\{ \frac{4 \sigma V_m}{d_p KT} \right\} \]

Eq. 7.31

where \( P_{eq} \) is designated as the equilibrium vapor pressure for a flat surface. From equation 7.31, the vapor pressure over a drop is shown to increases as the particle diameter decreases. Since the volatile and trace species are assumed to condense well after coalescence of the submicron particles has ceased, the area of the primary particles available for condensation will be dependent on the extent of agglomeration. The projected area of such agglomerates have been shown to be \( A_{agg} = n^{0.87} A_o \) where \( A_o \) is the cross-sectional area of a primary sphere and \( n \) is the number of such primary particles in the agglomerate (Medalin, 1967). In establishing the flux of condensable vapors to the submicron
particles, both the kelvin effect and the true area of the primary submicron particles will be accounted for. For the present calculations, the agglomerates are assumed to be composed of five primary particles (see section 7.2).

The model's predictions for the extent of supersaturation of sodium in the presence of the residual and submicron particles for various cooling rates are presented in Figure 7.11. For a low chlorine content coal such as Montana lignite, sodium sulfate is the thermodynamically favored vapor species over the temperature range at which the sodium is anticipated to condense (McNallan et. al., 1981). Furthermore, chemical state analysis by ESCA shows that sodium is present as sodium sulfate in the fume, section 6.4. Therefore, the present calculations for sodium are based on the assumption that sodium presides as sodium sulfate. The equilibrium vapor pressure for sodium sulfate is calculated assuming a pure condensed phase. Because of the complex thermochemistry involved, accounting for the formation of sodium silicate and other sodium bearing solutions will not be considered. The particle size distribution for the residual and submicron particles is based on the fly ash distribution obtained from the combustion of Montana lignite (45/53 um) at a furnace temperature of 1700 K in twenty percent oxygen in nitrogen. The rate at which the combustion products are cooled as they approach the water cooled collection probe was estimated from the temperature profiles in the
Cooling rate
1 - 5,000 K/sec
2 - 20,000 K/sec
3 - 40,000 K/sec

Figure 7.11 - Tendency for critical supersaturation of Na$_2$SO$_4$ as combustion products are cooled in the presence of residual and submicron particles.
furnace (see Figure 3.2) to range between 2,000 K/sec to 7,000 K/sec. Assuming all the sodium vaporizes during combustion, the sodium vapors are predicted to saturate at about 1400 K. As the gases are cooled below 1400 K at a rate of 5,000 K/sec, all the sodium is predicted to condense heterogeneously. Only at much higher cooling rates, 40,000 K/sec, is the partial pressure of sodium predicted to exceed the critical supersaturation partial pressure necessary for the onset of homogeneous nucleation. However, even at a cooling rate of 40,000 K/sec, over ninety percent of the sodium is still predicted to condensed heterogeneously before the criteria for homogeneous nucleation is satisfied. Like sodium, the other volatile and trace species are assumed to condense heterogeneously as the combustion products are cooled.

For diffusion-limited condensation the concentration dependence of those species which condense heterogeneously on the submicron particles have been shown to be inversely proportional to particle size. The concentration of Na, As, Sb, Fe, Ca, and Mg obtained from the INAA of discrete size classified samples of the submicron particles are plotted verses reciprocal diameter in Figure 7.12. The observation that the concentration dependence of As, Sb, and Na is best correlated by $d^{-1}$ relationship supports the model's prediction that the volatile and trace species condense heterogeneously as the gases are being cooled. The determination of
Figure 7.12 - Concentration of various elements in the size classified fume verses inverse diameter
the stratification of the various elements within the submicron particle by Auger spectroscopy show that the volatile trace species form the outermost surface layer of the submicron particles.

Under the combustion conditions examined, the volatile and trace species have been assumed to have totally vaporized due to their high vapor pressure (Quann, 1982). The discrepancy between the amount of the volatile species appearing with the submicron particles and that in the parent coal were initially attributed to the fact that some of the volatile and trace species will condense heterogeneously on the surface of residual fly ash particles. Evidence for the condensation of the volatile and trace species on the residual fly ash can be obtained by examining their concentration dependence on particle size. For diffusion-limited heterogeneous condensation, the concentration dependence of the volatile and trace species in the residual fly ash is predicted to be inversely proportional to particle diameter square (i.e., continuum regime Kn > 1). Figure 7.13 shows that a significant fraction of sodium and potassium in the residual fly ash is present as a result of heterogeneous condensation on these particles. However, from the concentration trend for both sodium and potassium it is evident that some of the sodium and potassium may not have totally vaporized during combustion. Despite their high volatility, the concentration of sodium and potassium for the very large
Figure 7.13 - Concentration of Na and K in the residual fly ash verses inverse diameter squared.
residual fly ash particles do not tend toward zero, instead their concentration appears to reach an asymptote. There is some question as to whether a condensation driving force is actually achieved in the experimental system for the volatile trace species. In the case of arsenic, for example, the partial pressure of arsenic in the sampling system at 500 K is $1.3 \times 10^{-9}$ atms. This is considerably less than the equilibrium vapor pressure of arsenic (as $\text{As}_2\text{O}_6$) at the coolest point in the system (60 C in the impactor), since the boiling point of arsenic (as $\text{As}_2\text{O}_6$) is 730.2 K (Weast et al., 1974). Yet, eighty to ninety percent of the arsenic in the coal is recovered with the ash in the cascade impactor. The fact that the arsenic deposits at all in the system implies a low arsenic activity in the solid phase. The high-temperature gas-phase chemistry of As has been shown to be dominated by the forms $\text{HAsO}_2 < \text{AsO} < \text{H}_3\text{AsO}_4$ (Farber and Srivastava, 1975). The very low concentration of arsenic in our sampling system precludes on kinetic grounds the formation of $\text{As}_2$ species during cooling, even though such species may become thermodynamically favored. Consequently, the acid forms of arsenic can be expected to dominate at lower temperatures. In this case, the mechanism of deposition could involve the reaction of the acid with bases such as MgO and CaO in the condensed phase. Similar considerations may apply to other volatile trace species as well (i.e., Sb). The rate of adsorption of gaseous species reacting at the surface of a spherical particle in the continuum regime is
\[ F_i(d) = \frac{\pi a D}{2.60 \lambda} \frac{P_i d^2}{d_p} \]  
Eq. 7.32

where \( a \) is the probability of reaction on collision. The number of molecules depositing on particle of size \( dp \) per unit mass of the particle can be expressed as

\[ \frac{F_i(d)}{\left( \rho_p \left( \frac{\pi}{6} \right) d_p^3 \right)} \propto \frac{1}{d_p^1} \]  
Eq. 7.33

Thus, the concentration dependence of a depositing species which is adsorption controlled in the continuum regime is expected to be inversely proportional to the particle diameter. Figure 7.14 shows that the concentration of some of the volatile trace species such as As and Sb are better correlated by the \( d^{-1} \) relationship than the \( d^{-2} \) relationship, confirming that the deposition of these species is adsorption-limited. Since, the concentration of As and Sb tend toward zero for the very large particles residual fly ash particles, these species can be assumed to have totally vaporized.

The concentration dependence of Na, K, As, and Sb in the residual fly ash confirms that the presences of the volatile and trace species in the residual fly ash is a result of condensation and/or adsorption. However, the
Figure 7.14 - Concentration of As and Sb in the residual fly ash verses inverse diameter
explanation for the magnitude of those species in the residual fly ash is not obvious, since the submicron particles should dominate as the sink for the condensing vapors because of the high specific surface area of the submicron particles relative to the residual fly ash particles.

The residual-mode distribution function has been shown to be more or less independent of the overall degree of ash vaporization, $\phi$, (section 5.1). Therefore, the specific flux to this mode is independent of the combustion conditions. However, the submicron-mode distribution function has been shown to be highly sensitive to the overall degree of ash vaporization. Since the submicron-mode obeys the self preserving size distribution, the area of the fume which determines the flux to this mode should vary as $\phi^{0.6}$. The conformation of the area dependence to $\phi^{0.6}$ for the submicron particles is clearly demonstrated in Figure 7.15. The competition between the primary spheres of the fume and the residual fly ash particles as a sink for the condensing vapors can be fully described in terms of the overall degree of ash vaporization, $\phi$. For diffusion-limited condensation, the distribution of the volatile species between the two modes can be estimated from the flux integral for the residual fly ash particles, equation 7.29, and the primary spheres of the fume, equation 7.30. As previously stated, the kelvin effect and the reduction in the area of the primary particles due to agglomeration will be accounted for
Figure 7.15 - Superficial area of fume with predictions for self-preserving size distribution
in the flux integral for the submicron particles.

A comparison between the predicted and experimental fraction of vaporized sodium appearing in the fume for various cooling rates is shown in Figure 7.16. The amount of sodium vaporized was estimated from the concentration trends for each condition, Figure 7.17. The fraction of sodium appearing in the submicron particles (i.e., fume) is shown to be fairly well predicted by a cooling rate of 2,000 K/sec which is the lower bound for the cooling rates estimated in the furnace. The increase in the fraction of sodium appearing in the fume as the amount of the total ash vaporized, $\phi$, is increased from less than one percent to over twenty percent can be attributed to the increase in the area of the fume by $0.6$. The variation in the prediction of sodium appearing in the fume with cooling rate can be attributed to the fact that at lower cooling rates the concentration of condensable vapor is shown to remain fairly close to the saturation vapor pressure (see Figure 7.11). Consequently, for low cooling rates, the potential for condensation, ($P_i - P_{eq,i}$), will be small enough that the kelvin effect will preferentially reduce the potential for condensation to the submicron particles. However, as the cooling rate is increased the supersaturation of the condensable vapor increases and the kelvin effect becomes less pronounced due to the increase in the potential for condensation.
Figure 7.16 - Fraction of sodium collected with the fume for various degrees of vaporization of the total ash.
Figure 7.17 - Concentration of Na in the residual fly ash versus inverse diameter squared
For adsorption-limited deposition, the amount of trace volatiles will be determined from the area integral.

\[ \int_{0}^{2} n(v) \pi d_{p}^{2} dv \]  
Eq. 7.34

For the residual ash particle mode, the particle size distribution function, \( n(v) \), is approximated numerically from the experimental data. The BET area measurements of the residual fly ash indicate that there is negligible internal surface. Consequently only the superficial area of the particles need to be considered. Thus the area integral becomes

\[ \sum_{k=0}^{7} n_{k} d_{k}^{2} = 6V \sum_{k=0}^{7} \phi_{k}/d_{K} \]  
Eq. 7.35

In transforming the size distribution function, \( n(v) \), of the submicron particles for self-preservation, the area integral for the submicron particles becomes

\[ \frac{6V}{d_{f}} \phi \]  
Eq. 7.36

where \( G = \int_{0}^{\eta} \psi(\eta) d\eta \)

The 2/3-moment of \( \psi(\eta) \) represented by \( G \) has the value 0.90. The reduction in the area of the primary particles due to agglomeration will be accounted for in the area integral for the submicron particles.
A comparison between the predicted and experimental fraction of As and Sb appearing in the fume for adsorption-limited deposition is shown in Figure 7.18. The elements As and Sb unlike sodium and potassium appear to have completely vaporized since their concentration tend to zero for the very large residual fly ash particles (see Figure 7.14). Therefore, the fraction of the input mass of these elements recovered with the fume is a direct measure of the fraction of these elements in the vapor phase depositing on the submicron particles. If the reactivity of the submicron particles and residual fly ash particles are equal, the submicron particles are predicted to be the dominate sink. Clearly, the fraction of As and Sb collected with the submicron particles is less than that predicted. However, if the reactivity of the submicron particles and residual fly ash particles differ significantly, the distribution of the depositing material can be expected to change accordingly. Chemical characterization of the submicron particles have shown the outer layers of the particles are mainly composed of SiO$_2$, Na$_2$SO$_4$, and K$_2$SO$_4$, while the surface of the residual particles will be partially composed of MgO and CaO since the deposition of the volatile species will only partially coat the outer surface of the residual fly ash particles. Consequently, for the hypothesis proposed for the deposition of arsenic, the reactivity of the residual fly ash particles should be greater than the reactivity of the submicron
Figure 7.18 - Fraction of As and Sb collected with the fume for various degrees of vaporization of the total ash

FRACTION OF TOTAL ASH VAPORIZED

FRACTION OF ELEMENT IN FUME

ADSORPTION CONTROL

\[ \zeta = 1 \]

\[ \zeta = 8 \]
particles. As shown in Figure 7.18, if the relative surface reactivity of the fume, $\zeta$, is eight times less than the residual fly ash, the predicted distribution curve looks very much like that found experimentally for As and Sb. Because of the complex thermochemistry involved the exact determination of the relative reactivity of the two particle modes is not possible. However, the results do indicate that the relative reactivity of the two particle modes will influence the fraction of the volatile trace species depositing on the submicron particles.

Magnesium, Iron, and Calcium are the species which condense to form the initial submicron particles where their concentration are relatively homogeneous due to the subsequent coagulation of various sized particles. While the concentration of those species which condense heterogeneously after coalescence has ceased will display a particle size dependence. Furthermore the elemental stratification of the submicron particle by auger spectroscopy has shown that those species which condense heterogeneously form the outer surface layers of the particles. The amount of volatile species condensing on the submicron particles has been shown to be highly sensitive to the rate at which the combustion products are cooled and the degree of total ash vaporization. In the case of the volatile trace species As and Sb whose concentration display the same particle size dependence as sodium in the submicron particles can be assumed to be highly enriched
on the outer surface of these particles. The amount of volatile trace species depositing on the submicron particles whose deposition has been shown to be adsorption-limited will be highly sensitive to the relative reactivity of the two particle mode.
CHAPTER EIGHT

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The factors governing the physico-chemical characteristics of the inorganic submicron particles produced by the combustion of coal have been examined by burning size-graded Montana lignite particles in a laminar flow drop-tube furnace at 1700 K. The particle combustion temperature achieved vary from 1800 K to 2800 K as the oxygen concentration in which the coal particles burn is increased from 5 percent to 100 percent. Separation of the submicron particles from the residual fly ash particles which are deposited out in the cascade impactor and the utilization of several collection schemes for these particles has provided the versatility necessary for accurate detailed characterization of the submicron particles.

Size fractionation of the ash yields a bimodel size distribution. The average size of the primary particles in the submicron mode varies from less than 50 angstroms to greater than 400 angstroms, depending on the combustion conditions. The submicron particles are produced by vaporization of the mineral matter species during combustion and
their subsequent recondensation. The amount of fume produced as metal oxide increases from 0.1 percent at 1800 K to 20 percent at 2800 K. The growth of the submicron particles is well predicted by classical coagulation theory where theory provides a good representation of the observed primary particle size as a function of residence time and degree of ash vaporization. In the early stages of coagulation the particles coalesce, but as the temperature in the vicinity of the particles decreases subsequent to the completion of combustion of the char and as the primary particle diameter increases, the coalescence rate decreases and the agglomerate produced appears as aggregates of spheres.

The chemical composition of the Montana lignite fume is dominated by MgO and CaO at all but the lowest particle combustion temperature (< 1900 K), apparently because the vaporization of these refractory oxides is augmented by their chemical reduction to the more volatile metal vapor in the locally reducing atmosphere within the burning char particle. The inorganic submicron particles are found to consist of a core of MgO, CaO, and FeO with an inner coating of silica and an outer coating of sodium, arsenic, and other trace metals. Furthermore, the concentration of silicon and the volatile and trace species which are found to make up the outer surface of the submicron particles show a sharp increase with decreasing particle size.
From a steady state one dimensional model the reoxidation of the vaporized reduced-state species of Mg, Ca, and Fe away from the char surface results in the supersaturation of these refractory oxides in the boundary layer of the burning char particle which is predicted to provide the necessary driving for the formation of a new condensed phase by homogeneous nucleation. Silicon deposition subsequently occurs as a probable consequence of the low rate of oxidation of the SiO vapors released by the burning coal particle. The volatile and trace species condense on the outer surface as the combustion products are cooled. Most of the ash surface is provided by submicron particles even though they constitute only a small fraction of the total ash. Both the residual and submicron particles are coated with a surface deposit of volatile (Na) and trace (As,Sb) elements. The distribution of the volatile elements between the two size modes of the ash is influenced by the amount of submicron particles produced during combustion and the rate at which the combustion products are cooled. However, in the case of the trace species, where an insufficient driving force for diffusion-controlled condensation exists, the surface deposition of these species is believed to be chemically controlled. Consequently, the distribution of the trace species between the two size modes is influenced by both the relative reactivity and surface area between the two size modes.
8.2 RECOMMENDATION

(A) A more detailed investigation of the time resolved growth studies should be conducted in order to facilitate a better understanding of the transition in the coagulation of the submicron particles from one of coalescence to agglomeration. The approach would be to examine the growth of the fume produced from other coals where the contribution from the refractory oxides of calcium and magnesium is much less pronounced than that in the fume produced from the combustion of Montana lignite. Focusing on those fumes rich in iron, coalescence should occur at much lower temperatures and between much larger particles.

(B) A more detailed investigation of the vaporization of the volatile constituents, such as sodium, needs to be examined, with specific emphasis on its activity in the various mineral forms. For the case of Montana lignite where sodium is atomicly dispersed, the extent of vaporization of sodium appears to be sensitive to the burnout time for the char despite the increase in char combustion temperatures associated with decreasing burning times. The present rational is that at higher temperatures the mineral inclusions will be molten and consequently, their interaction with the sodium will be greatly enhanced. In obtaining a better understanding of the thermochemistry and examining the extent of vaporization of sodium in different coals where the association of sodium is varied, a more fundamental under-
standing of the vaporization of sodium can be obtained.

(C) The competition between the condensation of the vaporized volatile species on the submicron particles versus the residual fly ash particles is predicted to be highly dependent on the rate at which the combustion products are cooled. In obtaining better control of the cooling rate for the combustion products, a better understanding of the competition between the two size modes as sinks for the volatile species can be obtained.

(D) The competition between the deposition of the trace species between the two size modes has been proposed to be dependent on the relative reactivity of the surfaces for the two size modes. The distribution of the trace species between the two size modes for the fly ash produced from different coals suggests that the relative reactivity between the two size modes is dependent on coal type. In characterizing the surfaces of the fly ash produced from the various coals of interest and obtaining a better understanding of the thermochemistry may facilitate a better understanding of the distribution for the trace species between the two size modes.
REFERENCES

Altericher, D., B.S. Thesis, MIT, Department of Chemical Engineering (1980)


Bender, B., Williams, D., and Notis, M., "Absorption Effects in STEM Microanalysis of Ceramic Oxides", J. American Ceramic Society, 63, 149-151 (1968)

Castleton, K., personnal communication, DOE, METC (1981)

Cliff, G., and Lorimer, G.W., J. Microscopy, 103 (1975)


Dictor, R., M.S. Thesis, MIT (1979)


Flagan, R.C., Seventh symposium (International) on Combustion, p. 97, The combustion Institute (1979)


Frenkel, J., Phys., Moscow, 9, 385 (1945)


Garret-Ried, T., Personal communication, M.I.T (1979)

Glassman, I., Am. Rocket Society Preprint 938-59 (1959)


Graham, S.C., and Homer, J.B., Faraday Symp., 1, 85 (1973)

Hall, E., Personnel communication (1978)


Heide, H., Z. Angew Phy. 15, 116 (1963)


Kingery, W.D., Introduction to Ceramics, John Wiley and Sons, New York (1965)

Knutson, E.D., and Whitby, K.T., "Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications", J.


Medalia, A.I., *J. Colloid Interface Sci.*, 24, 393 (1973)


Padro, D., personnal communication, MIT (1981)


Smith, I.W., Fuel, 57 (1978)


Sudenfield, L., personnel communication (1979)

Timothy, L., Ph.D. Thesis, Department of Chemical Engineering (1982)


Tixier, R., "Electron Probe Microanalysis of Thin samples", to be published in Microbeam analysis in biology, (1979)


Wagner, C., Riggs, W., Davis, L., Moulder, J., and


Worthey, D., personal communication, Kevex Corporation (1980)