NOTE TO USERS

The original manuscript received by UMI contains pages with slanted and indistinct print. Pages were microfilmed as received.

This reproduction is the best copy available

UMI
REMOVAL OF SULFUR DIOXIDE AND NITRIC OXIDE BY LIGNITE
AND VARIOUS OTHER LIGNITE-DERIVED ADSORBENTS

A thesis
Submitted to the College of Graduate Studies and Research
in partial fulfillment of the requirements
for the Degree of
Doctor of Philosophy
in the
Department of Chemical Engineering
University of Saskatchewan
by

GOUTAM CHATTOPADHYAYA

August, 1995

Copyright © 1995 Goutam Chattopadhyaya

The University of Saskatchewan claims copyright in conjunction with the author. Use shall not be made of material contained without proper acknowledgment.
The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author’s permission.

L’auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L’auteur conserve la propriété du droit d’auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-32807-4
UNIVERSITY OF SASKATCHEWAN
College of Graduate Studies and Research
SUMMARY OF DISSERTATION

Submitted in partial fulfillment
of the requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY
by
Goutam Chattopadhyaya

Department of Chemical Engineering
University of Saskatchewan
1995

Examinng Committee:

Dr. R.B. McKercher

Dr. J. Postlethwaite

Dr. N. N. Bakhshi
Dr. D.G. Macdonald
Dr. G.A. Hill
Dr. D. Russell

Dean/Associate Dean/Dean's Designate,
Chair College of Graduate Studies and Research
Chair of Advisory Committee, Department of
Chemical Engineering

Supervisor, Department of Chemical Engineering
Co-supervisor, Department of Chemical Engineering
Department of Chemical Engineering
Department of Chemistry

External Examiner:

Dr. P. R. Bishnoi
Department of Chemical and Petroleum Engineering
University of Calgary
Calgary, Alberta
T2N 1N4
Removal of Sulfur Dioxide and Nitric Oxide by Lignite and Various Other Lignite-Derived Adsorbents

The purpose of this work was to develop an adsorbent from Saskatchewan lignite that is efficient for the removal of sulfur dioxide (SO₂) and nitric oxide (NO) from flue gases and, also, to develop the models for their removal processes.

The development of the adsorbents was achieved by optimizing a number of adsorbent preparation parameters using extensive physical characterization of the adsorbents as well as their SO₂ and NO removal performance as the tool.

The carbonization of lignite to produce char and subsequent activation of char to produce activated carbon (AC) as well as the SO₂ or NO removal performance evaluation were performed in stainless steel fixed-bed reactors. The operating conditions for carbonization were: carbonization temperature, 350-550°C; time, 30-120 min. Those for activation were: activation temperature, 550-750°C; time, 15-45 min; activation agent, steam and carbon dioxide (CO₂). SO₂ and NO removal performance evaluation experiments used: particle size, 2-5.6 mm; adsorption temperature, 75-175°C; residence time, 4-10 sec; influent SO₂ concentration, 1000-5000 ppm; influent NO concentration, 400-1100 ppm; O₂ concentration, 0-6.5 vol%.

SO₂ removal performance depended strongly on the fraction of supermicropores in the adsorbents, types of metals impregnated, SO₂ residence time and influent concentration, and on the presence of O₂. Maximum SO₂ removal (86 mg/g) was achieved with the reduced Cu/AC adsorbent.

On the other hand, NO removal efficiency depended on the surface area of the adsorbent, type and valence state of the metal impregnated, and presence of O₂. High NO
removal efficiency was achieved with reduced Cu/AC (46%) and Ni/AC (47.5%) adsorbents in the presence of O₂.

For the first time, a kinetic model has been developed for predicting NO removal from a mixture of NO-N₂ over char and AC adsorbents. Also, an adsorption model has been developed for the removal of SO₂ over lignite.

The results from these studies have also shown, for the first time, that methanol can be used for complete removal of NO in the absence of O₂ over a Mn-promoted co-precipitated Cu-Al catalyst at temperatures as low as 200°C.
In presenting this thesis in partial fulfilment of the requirements for a Postgraduate degree from the University of Saskatchewan, I agree that the libraries of this University may make it freely available for inspection. I further agree that permission for copying of this thesis in any manner, in whole or in part, for scholarly purposes may be granted by the professor or professors who supervised my thesis work or, in their absence, by the Head of the Department or the Dean of the College in which my thesis work was done. It is understood that any copying or publication or use of this thesis or parts thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of Saskatchewan in any scholarly use which may be made of any material in my thesis.

Requests for permission to copy or to make other use of material in this thesis in whole or part should be addressed to:

Head of the Department of Chemical Engineering
University of Saskatchewan
Saskatoon, Saskatchewan S7N 0W0
My Parents, Pradip and Mamata Chatterjee

and

Dr. Narendra N. Bakhshi and Mrs. Nirmal Bakhshi
ACKNOWLEDGMENTS

I am thankful for the guidance of Drs. N. N. Bakhshi and D. G. Macdonald throughout this program of further study; without their supervision this program of research would not have been possible. I also wish to mention Dr. D. Smith, Senior Research Engineer at Saskatchewan Power Corporation, Regina, SK, for his helpful discussions and suggestions.

I am indebted to the other members of the examining committee, Drs. M. N. Esmail, G. A. Hill and D. Russell for their helpful discussions and suggestions.

I am very much thankful to Dr. M. N. Esmail for his valuable guidance and suggestions during the modeling and simulation part of my work. I also am grateful to Dr. D.-Y. Peng for letting me use his computer for typing my thesis.

Thanks also go to Dr. Sanjoy Saha, Dr. Khosrow Nikkah, Richard Evitts, Hani Ali, Kanad Roy, Dr. Hemant Sinha and Dr. Raphael Idem for their assistance and friendship.

I thank Mr. T. Wallentiny for his technical assistance and Mr. A. Leyland and Mr. Rick Elvin for construction of the experimental apparatus.

I appreciate the cooperation and useful discussions of Dr. R. Sharma, Dr. M. Bisaria, Dr. A. K. Dalai, Dr. Sai Katikaneni, Dr. John Adjaye, Dr. Raphael Idem, Miss Anita Johnson.

I am grateful to the Saskatchewan Power Corporation and University of Saskatchewan for awarding me a scholarship for the duration of this study.

Last, but by no means least, thanks go to my parents Pradip and Mamata Chatterjee, my supervisor Dr. Narendra Nath Bakhshi and his wife Mrs. Nirmal Bakhshi who have supported me in many different ways. This Ph.D. thesis is dedicated to them.
ABSTRACT

The purpose of this work was to develop an adsorbent from Saskatchewan lignite efficient for the removal of sulfur dioxide (SO$_2$) and nitric oxide (NO) from power plant flue gases and also to develop the theoretical models for their removal processes.

The development of the lignite-based adsorbents was achieved by optimization in various phases of a number of adsorbent preparation parameters. Extensive physical characterization and SO$_2$ and NO removal performance evaluation were performed for each phase to provide the tools for this optimization process.

The base material used in this program was Saskatchewan lignite. In this work, the objective was to improve the adsorption performance of lignite by optimizing carbonization, activation and metal impregnation process parameters.

The carbonization of lignite to produce char, subsequent activation of char to produce activated carbon (AC) and the SO$_2$ and NO removal performance evaluation were performed separately in stainless steel fixed-bed reactors. The operating conditions for carbonization were: carbonization temperature, 350-550°C; carbonization holding time, 30-120 min. Those for activation were: activation temperature, 550-750°C; activation time, 15-45 min; activation agent, steam and carbon dioxide (CO$_2$). Copper (Cu), cobalt (Co), nickel (Ni) and iron (Fe) impregnated activated carbons were prepared by impregnating activated carbon support with aqueous solutions of respective metal nitrates. For SO$_2$ and NO performance evaluation experiments the operating conditions were: particle size, 2-5.6 mm; adsorption temperature, 75-175°C; residence time, 4-10 sec; influent SO$_2$ concentration, 1000-5000 ppm; influent NO concentration, 400-1100 ppm; O$_2$ concentration, 0-6.5 vol%.

SO$_2$ removal performance depended strongly on the fraction of supermicropores in the adsorbents, types of impregnated metals, residence time as well as influent SO$_2$
concentration, and the presence or absence of $O_2$. Maximum $SO_2$ removal efficiency (86 mg/g) was obtained from the reduced Cu/AC adsorbent. By contrast, NO removal efficiency depended on the surface area of the adsorbent, type and valence state of the impregnated metal, influent concentration of NO and the presence and absence of $O_2$. High NO removal efficiency was achieved with reduced Cu/AC (46%) and Ni/AC (47.5%) adsorbents in the presence of $O_2$.

For the first time, a kinetic model has been developed that can predict NO removal from a mixture of NO-$N_2$ over char and AC adsorbents. An adsorption model has also been developed for the removal of $SO_2$ over lignite.

It has been shown for the first time that methanol can be used for the complete removal of NO in the absence of $O_2$ over a Mn-promoted co-precipitated Cu-Al catalyst at temperatures as low as 200°C.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xv</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xvii</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Problem identification</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Project objective</td>
<td>6</td>
</tr>
<tr>
<td>2. LITERATURE REVIEW</td>
<td>10</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>10</td>
</tr>
<tr>
<td>2.2 Formation of nitric oxides and sulfur dioxide</td>
<td>10</td>
</tr>
<tr>
<td>2.3 Control technologies for nitric oxides</td>
<td>12</td>
</tr>
<tr>
<td>2.3.1 Wet processes</td>
<td>14</td>
</tr>
<tr>
<td>2.3.2 Dry processes</td>
<td>15</td>
</tr>
<tr>
<td>2.4 Control technologies for sulfur dioxide</td>
<td>19</td>
</tr>
<tr>
<td>2.4.1 Non-regenerative alkaline processes</td>
<td>20</td>
</tr>
<tr>
<td>2.4.2 Regenerative alkaline processes</td>
<td>21</td>
</tr>
<tr>
<td>2.4.3 Furnace injection</td>
<td>22</td>
</tr>
<tr>
<td>2.4.4 Regenerative organic absorption</td>
<td>22</td>
</tr>
<tr>
<td>2.4.5 Catalysis</td>
<td>22</td>
</tr>
<tr>
<td>2.4.6 Regenerative solid adsorption</td>
<td>23</td>
</tr>
<tr>
<td>2.5 Simultaneous removal of sulfur dioxide and nitric oxides</td>
<td>23</td>
</tr>
<tr>
<td>2.5.1 NOXSO process</td>
<td>24</td>
</tr>
</tbody>
</table>
2.5.2 SNO\textsubscript{x} process 24
2.5.3 DeSNO\textsubscript{x} process 25
2.5.4 Copper oxide process 25
2.5.5 Carbon adsorbent technology 26

2.6 Selection of lignite for preparation of activated carbon 27
2.6.1 Structure of coal 27
2.6.2 Criteria for selection of coal for activated carbon manufacture 30

2.7 Carbonization and activation of lignite 30
2.7.1 Selection of carbonization process parameters 31
2.7.2 Activation of char 31
2.7.3 Metal-impregnated activated carbons 33

2.8 Physical characterization of coal and coal-derived microporous adsorbents 35
2.8.1 Characterization of lignite and lignite-derived adsorbents 35
2.8.1.1 Techniques available for determining microstructure of coal 35
2.8.1.2 Physical adsorption technique for determining microstructure 36
2.8.2 Fourier transformed infrared spectroscopy (FT-IR) in fuel science 38

2.9 Kinetic modeling 39
2.9.1 Modeling of sulfur dioxide adsorption 39
2.9.2 Modeling of nitric oxide removal 41
3. EXPERIMENTAL

3.1 Scope

3.2 Preparation of adsorbents

3.2.1 Preparation of lignite

3.2.2 Preparation of chars

3.2.2.1 Experimental rig for the preparation of the chars

3.2.2.2 Typical carbonization run

3.2.2.3 Analysis of gaseous product evolved during carbonization

3.2.3 Preparation of activated carbon

3.2.3.1 Experimental rig used for activation

3.2.3.2 Typical activation run

3.2.4 Preparation of metal-impregnated activated carbon

3.2.4.1 Materials

3.2.4.2 Impregnation procedure

3.3 Characterization of adsorbents

3.3.1 Physical characterization of lignite

3.3.2 Physical characterization of char and activated carbon

3.3.3 Physical characterization of metal-impregnated activated carbons

3.3.4 Carbon-hydrogen-nitrogen elemental analysis

3.3.5 Temperature programmed reduction studies of metal-impregnated activated carbons

3.3.6 (FT-IR) spectroscopic analysis

3.4 Adsorbent performance evaluation studies
3.4.1 Experimental rig for the evaluation of the adsorbent 57
3.4.2 Operating variables for adsorption experiments 59
3.4.3 Procedure for evaluation of adsorbent performance 60
3.4.4 Analysis of adsorbent effluent stream 60
3.4.5 Construction of breakthrough curves 62

3.5 Experiments to examine the potential of nascent hydrogen for NO\textsubscript{x} reduction 62
3.5.1 Experimental rig for the evaluation of the adsorbent performance 63
3.5.2 Operating variables for NO\textsubscript{x} reduction experiments 63
3.5.3 Procedure for evaluation of catalyst performance for the NO\textsubscript{x} reduction 65

4. RESULTS AND DISCUSSION 66
4.1 Phase 1: Preliminary work 67
4.1.1 Physical characterization of lignite 67
4.1.1.1 Effect of adsorbate 68
4.1.1.2 Effect of degassing temperatures 70
4.1.2 Gas chromatographic analysis 72
4.2 Phase 2: Preparation of char and activated carbon from lignite and their characterization 75
4.2.1 Adsorption of sulfur dioxide by lignite 75
4.2.1.1 Effect of residence time 77
4.2.1.2 Effect of influent sulfur dioxide concentration 79
4.2.1.3 Effect of adsorption temperature 80
4.2.1.4 Effect of lignite particle size 83
4.2.1.5 Statistical design and modeling of sulfur dioxide adsorption by lignite

4.2.1.6 Selection of operating variables for subsequent sulfur dioxide adsorption experiments

4.2.2 Carbonization of lignite and physical characteristics of chars

4.2.2.1 Effect of carbonization temperature on gas, char and tar yield

4.2.2.2 Effect of carbonization temperature on \( \text{CO}_2, \text{CO} \) and \( \text{H}_2 \) yield

4.2.2.3 Effect of carbonization temperature on hydrocarbon yield

4.2.2.4 Effect of carbonization temperature on the physical properties of char

4.2.2.5 Effect of carbonization holding time on gas, char and tar yield

4.2.2.6 Effect of carbonization holding time on hydrocarbon yield

4.2.2.7 Effect of carbonization holding time on the physical properties of chars

4.2.2.8 Optimization of the carbonization parameters

4.2.3 Sulfur dioxide adsorption by chars

4.2.4 Activation of char

4.2.4.1 Effect of activation temperature on the
physical properties of activated carbons 113

4.2.4.2 Effect of activation time on physical properties of activated carbons 122

4.2.4.3 Summary 123

4.2.4.4 Comparison of microporosity of lignite, char and activated carbon 124

4.2.5 Sulfur dioxide adsorption by activated carbons 124

4.2.6 Chemical characterization of adsorbents 128

4.2.6.1 FT-IR spectroscopic analysis of lignite, char and activated carbons 128

4.2.6.2 Elemental analysis of lignite, char and activated carbons 132

4.3 Phase 3: Preparation and characterization of metal-impregnated activated carbons 135

4.3.1 Physical characterization of metal-impregnated activated carbons 135

4.3.2 Temperature programmed reduction of metal-impregnated activated carbons 141

4.4 Phase 4: Adsorptive and reactive removal of sulfur dioxide by metal-impregnated act. carbon 144

4.4.1 Sulfur dioxide removal performances of various metal-impregnated activated carbons 144

4.4.2 Effect of valence state of the active metal 149

4.4.3 Effect of oxygen on the sulfur dioxide removal 149

4.4.4 Reaction mechanism of the removal of sulfur dioxide 155
4.5 Phase 5: Adsorptive and reactive removal of nitric oxide by lignite and various lignite-derived adsorbents

4.5.1 Nitric oxide removal performances of lignite, char and activated carbons

4.5.2 Nitric oxide removal performances of metal-impregnated activated carbons

4.5.3 Effect of valence state on the nitric oxide removal performances of the metal-impregnated activated carbon adsorbents

4.5.4 Effect of oxygen on nitric oxide removal performance

4.6 Phase 6: Simultaneous removal of sulfur dioxide and nitric oxide

4.7 Phase 7: Kinetic modeling

4.7.1 Modeling and simulation of sulfur dioxide adsorption on lignite

4.7.2 Derivation of rate models for the removal of nitric oxide by carbon-based adsorbents

4.7.2.1 Reaction mechanism for the removal of NO by lignite and lignite-derived adsorbents

4.7.2.2 Rate modeling

4.8 Phase 8: Catalytic reduction of NO by in-situ decomposition and steam reforming of methanol

5. CONCLUSIONS

6. RECOMMENDATIONS
7. REFERENCES

APPENDIX A: Sample Calculations

APPENDIX B: Chromatographic analysis of sulfur dioxide and nitric oxide

APPENDIX C: Computer program for simulating kinetic model for NO removal on char and activated carbon adsorbents.
LIST OF TABLES

Table 2.1  Classification of Carbonization Process on the Basis of Carbonization Temperature and Heating rate  32
Table 4.1  Physical Characteristics of Lignite Estimated From CO₂ and N₂ adsorption  69
Table 4.2  Sulfur Dioxide Breakthrough Time and Adsorption Capacity on Lignite As a Function of Particle Size, Adsorption Temperature, Influent Sulfur Dioxide Concentration and Residence time  76
Table 4.3  Physical Characteristics of Chars Estimated From CO₂ Adsorption  96
Table 4.4  Sulfur Dioxide Adsorption Capacity of Lignite, Char and Activated Carbon on the Basis of 1 g of the Starting Material (Lignite)  111
Table 4.5  Physical Characteristics of Activated Carbons Estimated From CO₂ Adsorption  114
Table 4.6  Elemental Carbon-Hydrogen-Nitrogen Analysis of Lignite, Char and Activated Carbons  133
Table 4.7  Physical Characteristics of Metal-Impregnated Activated Carbons Estimated From CO₂ Adsorption  136
Table 4.8  Sulfur Dioxide Breakthrough Time on Various Metal-Impregnated Activated Carbon Adsorbents  147
Table 4.9  Overall Nitric Oxide Removal Efficiencies of Various Lignite-Derived Adsorbents  161
Table 4.10  Nitric Oxide Breakthrough Time on Various
<table>
<thead>
<tr>
<th>Table 4.11</th>
<th>Reduction of Nitric Oxide Using Methanol As the Reductant in the Absence of Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 4.12</td>
<td>Reduction of Nitric Oxide Using Methanol As the Reductant in the Presence of Oxygen</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Available Techniques to Decrease Emission of Nitric Oxide</td>
<td>13</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Typical Cross-bonded Structure of High Volatile Coals</td>
<td>29</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>The Mechanism of NO-NH₃ Reaction on Vanadium Oxide as Proposed by Miyamoto Et. Al. (1982)</td>
<td>42</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Proposed Sequence of Reactions for the Reduction of NO Over a Supported Vanadia Catalyst to Form N₂, H₂O and N₂O as Proposed by Janssen Et. Al. (1987a; b)</td>
<td>43</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Process Flow Diagram of the Experimental Rig for Carbonization of Lignite and Activation of Char.</td>
<td>48</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Conventional Temperature Programmed Reduction (TPR) /Temperature Programmed Desorption (TPD) System</td>
<td>55</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Process Flow Diagram of the Experimental Rig for Sulfur Dioxide and Nitric Oxide Adsorption Experiments</td>
<td>58</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Schematic Diagram of the Experimental Rig for Nitric Oxide Reduction Experiments</td>
<td>64</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Typical Chromatogram Obtained From Gas Chromatographic Analysis of Nitric Oxide</td>
<td>74</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Effect of Residence Time on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite</td>
<td>78</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Effect of Influent Sulfur Dioxide Concentration on Its Breakthrough Profile in a Bed of Lignite</td>
<td>81</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Effect of Adsorption Temperature on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite</td>
<td>82</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Effect of Particle Size on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Effect of Carbonization Temperature on Char, Tar and Gas Yields From Lignite Coal</td>
<td></td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Effect of Carbonization Temperature on the Yield of Non-hydrocarbon Gases Such As CO, CO₂ and H₂ From Lignite Coal</td>
<td></td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Effect of Carbonization Temperature on the Yields of Hydrocarbon Gases From Lignite Coal</td>
<td></td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>Micropore Surface Area (Estimated by Dubinin-Astakhov Method) ofChars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min</td>
<td></td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Micropore Volume (Estimated by Dubinin-Astakhov Method) ofChars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min</td>
<td></td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>Median Pore Diameter (Estimated by Horvath-Kawazoe Method) ofChars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min</td>
<td></td>
</tr>
<tr>
<td>Figure 4.12</td>
<td>Comparison of Micropore Size Distribution ofChars Prepared at Different Carbonization Temperatures With That of Lignite (Points for the Char, Prepared at 475°C, and that for Lignite Are Connected by Solid Lines)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.13</td>
<td>Effect of Carbonization Holding Time on the Yields of Char, Tar and Gas From Lignite Coal</td>
<td></td>
</tr>
<tr>
<td>Figure 4.14</td>
<td>Effect of Carbonization Holding Time on the Yields of Hydrocarbon Gases From Lignite Coal</td>
<td></td>
</tr>
<tr>
<td>Figure 4.15</td>
<td>Effect of Carbonization Temperature on the Sulfur Dioxide Adsorption Capacity of Char</td>
<td>108</td>
</tr>
<tr>
<td>Figure 4.16</td>
<td>Comparison of the Sulfur Dioxide Breakthrough Profiles of Char Prepared at Different Carbonization Temperatures With That of Lignite</td>
<td>110</td>
</tr>
<tr>
<td>Figure 4.17</td>
<td>Micropore Surface Area (Estimated by Dubinin-Astakhov Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min</td>
<td>115</td>
</tr>
<tr>
<td>Figure 4.18</td>
<td>Micropore Volume (Estimated by Dubinin-Astakhov Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min</td>
<td>117</td>
</tr>
<tr>
<td>Figure 4.19</td>
<td>Median Pore Diameter (Estimated by Horvath-Kawazoe Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min</td>
<td>118</td>
</tr>
<tr>
<td>Figure 4.20</td>
<td>Comparison of Micropore Size Distribution of Carbon Dioxide Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min</td>
<td>120</td>
</tr>
<tr>
<td>Figure 4.21</td>
<td>Comparison of Micropore Size Distribution of Steam Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min</td>
<td>121</td>
</tr>
<tr>
<td>Figure 4.22</td>
<td>Micropore Size Distribution of Lignite, Char (Prepared at 475°C for 120 min) and Activated Carbons (Prepared at 650°C for 15 min by Steam and Carbon Dioxide Activation)</td>
<td>125</td>
</tr>
</tbody>
</table>
Figure 4.23  Effect of Activation Temperature and Agent on the
Sulfur Dioxide Adsorption Capacity of Activated Carbons  126

Figure 4.24  Fourier-Transformed Infrared (FT-IR) Spectrum of Lignite  129

Figure 4.25  Fourier-Transformed Infrared Spectrum of Char (Prepared
at 475°C for 120 min)  130

Figure 4.26  Comparison of Fourier-Transformed Infrared Spectras
of Char (Prepared at 475°C for 120 min) and
Activated Carbons (Prepared at 650°C for 15 min
by Steam and Carbon Dioxide Activation).  131

Figure 4.27  Comparison of Cumulative Micropore Volume of
Calcined and Uncalcined Iron, Copper, Cobalt
and Nickel Impregnated Activated Carbons
With That of Activated Carbon Alone  138

Figure 4.28  Comparison of Differential Micropore Volume of
Calcined and Uncalcined Iron Impregnated Activated
Carbon With That of Activated Carbon Alone  139

Figure 4.29  Comparison of Differential Micropore Volume of
Calcined and Uncalcined Copper Impregnated
Activated Carbon With That of Activated Carbon Alone  140

Figure 4.30  Temperature Programmed Reduction Profile of
Iron Impregnated Activated Carbon  142

Figure 4.31  Temperature Programmed Reduction Profile of Copper
Impregnated Activated Carbon  143

Figure 4.32  Sulfur Dioxide Breakthrough Profiles on Activated carbon
and Metal Impregnated Activated Carbons in the Absence
of Oxygen  146
Figure 4.33  Sulfur Dioxide Breakthrough Profiles on Reduced and Unreduced Copper Impregnated Activated Carbons in the Absence of Oxygen  
150

Figure 4.34  Sulfur Dioxide Breakthrough Profiles on Reduced and Unreduced Copper Impregnated Activated Carbons in the Presence of Oxygen  
151

Figure 4.35  Typical Sulfur Dioxide Breakthrough Profiles on Lignite in the Presence and Absence of Oxygen  
152

Figure 4.36  Sulfur Dioxide Breakthrough Profiles on Reduced and Unreduced Copper and Iron Impregnated Activated Carbons, As Well As Activated Carbon Alone, in the Presence of Oxygen  
154

Figure 4.37  Nitric Oxide Breakthrough Profiles on Lignite, Char and Steam Activated Carbons in the Absence of Oxygen  
160

Figure 4.38  Nitric Oxide Breakthrough Profiles on Steam Activated Carbon and Unreduced Iron Impregnated Activated Carbon in the Absence of Oxygen  
166

Figure 4.39  Nitric Oxide Breakthrough Profiles on Reduced and Unreduced Iron Impregnated Activated Carbon in the Absence of Oxygen  
167

Figure 4.40  Nitric Oxide Breakthrough Profiles on Activated Carbon, and, Reduced and Unreduced Iron Impregnated Activated Carbons in the Absence of Oxygen  
168

Figure 4.41  Nitric Oxide Breakthrough Profiles on Reduced Iron, Copper, Cobalt and Nickel Impregnated Activated Carbons in the Presence of Oxygen  
171
Figure 4.42 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Lignite in the Presence of Oxygen

Figure 4.43 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Reduced Iron Impregnated Activated Carbon in the Presence of Oxygen

Figure 4.44 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Reduced Copper Impregnated Activated Carbon in the Presence and Absence of Oxygen

Figure 4.45 Effect of $\alpha$ (Index for Axial Dispersion in the Column) on Predicted Sulfur Dioxide Breakthrough Profile on Lignite for a Specified Value (0.7) of $\lambda$ (Index for Adsorption Equilibrium)

Figure 4.46 Effect of $\lambda$ on Predicted Sulfur Dioxide Breakthrough Profile on Lignite for a Specified Value (5.0) of $\alpha$

Figure 4.47 Sulfur Dioxide Breakthrough Curve on Lignite: Theoretical and Experimental Results

Figure 4.48 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Rate Constant of Adsorption, $K_a$

Figure 4.49 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Rate Constant of Surface Reaction, $K_c$

Figure 4.50 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Residence Time, $\tau$
Figure 4.51  Nitric Oxide Breakthrough Curves on Char and Activated Carbon: Theoretical and Experimental Results 194
Notation

$A_i$  Reactant $i$
$C_i$  Concentration of $i$
$C^*$  Concentration of active sites
$k$  Rate constant
$K$  Adsorption equilibrium constant
$m_c$  Mass of catalyst
$P$  Pressure
$R_i$  Transformation rate of $i$
$S_i$  Active sites
$T$  Temperature
$t$  Time
$V_r$  Volume of the reactor
$\tau$  Space time

Subscript

a, ads  Adsorption
c  Catalyst
d  Desorption
i  Reactant
o  Initial
s  Carrier steady state
v  Volume
1. Introduction

1.1 Introduction

Sulfur dioxide (SO$_2$) and nitric oxide (NO) are major air pollutants whose emissions have been linked to the formation of acid rain, urban smog and many other undesirable environmental hazards. NO also contributes to the ozone problem. Fossil-fuel fired power plants, auto exhausts and other industrial emissions are the major sources of these two air pollutants.

In the case of SO$_2$, a variety of flue gas desulfurization techniques are available for its removal from flue gases. These can be broadly classified into four general categories: (i) absorption of SO$_2$ in liquids, (ii) absorption of SO$_2$ by moist particles, (iii) gas phase conversion of SO$_2$, and (iv) sorption of SO$_2$ by solids.

For NO, control technologies can be divided into two categories: (i) clean techniques; and (ii) clean-up techniques or flue gas treatment. Much work has been done on the development of clean techniques; possible clean techniques are the control of the nitrogen content of the fuel, modification of the burner and the combustion process. These techniques are not yet widely used commercially. The clean-up or flue gas treatment technologies that are currently being practiced generally involve either a wet or a dry process. Wet processes can be divided into three categories: (i) gas phase absorption of NO, (ii) gas phase oxidation of NO and subsequent absorption of NO$_2$ and (iii) chelation of NO with ethylenediamine tetraacetate (EDTA). Dry processes can be divided into the following categories: (i) selective catalytic reduction of NO, (ii) non-selective catalytic reduction of NO, (iii) selective non-catalytic reduction of NO, (iv) non-selective non-catalytic reduction of NO, (v) adsorption of NO on solids and (vi) radiation for decomposing NO.
1.2 Problem identification

Most of the flue gas desulfurization techniques which are currently used commercially are based on the absorption of \( \text{SO}_2 \) on various metal oxides or hydroxides (Kohl and Riesenfeld, 1979); for example, one of the most dominant and reliable processes for handling \( \text{SO}_2 \) in flue gas is limestone scrubbing or injection. This results in the production of large amounts of calcium sulfate which does not attract much market value and thus is treated as a waste.

To circumvent this problem, various processes, such as the Wellman-Lord process, which are based on adsorption and catalytic reaction, are available to convert \( \text{SO}_2 \) into elemental sulfur (S). This is still not a very attractive process since S does not command high market value. However, a few processes are available which convert \( \text{SO}_2 \) into a more useful product like sulfuric acid. These processes use catalysts such as vanadium pentoxide \((V_2\text{O}_5)\) and copper oxide \((\text{CuO})\) supported on alumina \((\text{Al}_2\text{O}_3)\) and operate at temperatures around 425°C. In addition to the complexity of these processes, water vapor, which is one of the main components of flue gases, has been found to decrease the catalytic activity of these catalysts. Since flue gas temperature at the point of flue gas cleaning is low, it is desirable to carry out the \( \text{SO}_2 \) removal process at low temperatures because operation at high temperatures will require flue gas reheating. Recent literature suggests that activated carbon could be used as an adsorbent and catalyst for the removal of \( \text{SO}_2 \) at low temperature (Richter et. al., 1985; 1990).

In the case of NO, the processes available have various drawbacks. For example, the wet processes which are based on absorption principles have the disadvantage that NO is insoluble in water and has to be oxidized to nitrogen dioxide \((\text{NO}_2)\) before absorption can take place. This makes wet processes very expensive. In addition, the by-products formed from \( \text{NO}_2 \) absorption contain nitrates and nitrites.
which present disposal problems. Therefore, dry systems seem to be the best choice for the removal of nitric oxides.

In the case of dry processes, selective catalytic reduction is considered to be the best. In the selective catalytic reduction (SCR) process, NO is reduced by a reducing agent to nitrogen and water at 300-450°C over a catalyst. The main drawbacks of SCR technology are: (i) high optimum operating temperature of the catalyst bed, (ii) poisoning of the catalyst by SO₂ (which is usually present in the flue gas), and (iii) leakage of ammonia, which is, by itself, another air pollutant.

To circumvent this problem, various other systems have been proposed and tested which use different combinations of a wide variety of reducing agents (H₂, CH₄, CO and hydrocarbons) and catalysts (supported metal oxides, zeolite based catalysts, noble metal based catalysts) (Bosch and Janssen, 1987). However, the operating temperatures required to maintain catalyst activity are still high. The high operating temperature for SCR catalysts restricts the location of the SCR unit in the power plant and requires flue gas reheating. Therefore, what is needed is a process or a catalyst which can work at low operating temperatures, otherwise, extensive flue gas reheating will be required. In the recent literature (e.g. Richter, 1990), activated carbon has been used as a catalyst for the SCR of NO using ammonia at low temperatures ranging from 90 to 190°C.

In actual operations flue gases containing both NO and SO₂ are cleaned by stepwise processes to remove NO and SO₂ by combining SCR technology with flue gas desulfurization (DeSOₓ) technology. For example, in coal-fired power plants, the SCR process is generally used to remove NO while limestone injection is used to remove SO₂. However, what is lacking is a regenerative process that simultaneously removes both NO and SO₂ in one step at low temperature preferably without using a corrosive reducing agent. The use of activated carbon offers an alternative for the simultaneous removal of NO and SO₂. In one such process, developed by BF-udhe
(Germany), \( \text{SO}_2 \) is removed in the first charcoal bed of a two-stage adsorber by adsorption and NO is catalytically removed with ammonia in the second bed. The active charcoal used in this process is prepared from hard coal.

The activated carbon process has the added advantage that it operates at low temperatures and is cheap compared to the combined cost of the SCR processes using \( \text{V}_2\text{O}_5 \) based catalysts for NO removal, and the limestone scrubbing process for \( \text{SO}_2 \) removal. However, it is possible to make the activated carbon based processes even more economical if a cheaper source of activated carbon could be found. In Saskatchewan, there are large deposits of lignite which could provide a cheap and effective source of activated carbon for the removal process. Although considerable research work has been carried out on the adsorptive removal of \( \text{SO}_2 \) and selective catalytic removal of NO on various activated carbons, very little information is available in the literature on the adsorption characteristics of \( \text{SO}_2 \) and NO on lignite and other lignite-derived adsorbents.

In the literature (Davini, 1990) the adsorption capacity of activated carbons has been attributed to their physico-chemical properties such as porosity and oxygenated surface groups on the carbon even though the correlation of the adsorption capacity with some of those properties such as BET surface area proved to be unsuccessful. It is also known that physico-chemical properties of activated carbons are controlled by independent variables such as carbonaceous precursors and the methods of preparation. Considerable information is available on the preparation of activated carbons from different carbonaceous precursors (Mantell, 1977; Hassler, 1974) such as bituminous coal and coconut shell. It has also been shown (Stoeckli and Ballerini, 1991) that with the exception of the inherent structural characteristics of the carbonaceous precursors, carbonization and activation processes play a major role in the evolution of microporosity; however, it is still not clear how carbonization and activation process parameters affect the final adsorbent characteristics.
Consequently, the relationship between carbonization and activation process parameters and the adsorbents characteristics is not clearly understood. Under these conditions, it is extremely difficult to design a carbon adsorbent with the objective of obtaining the highest possible adsorption characteristics.

As mentioned before the literature indicates that an entirely different kind of catalysts such as CuO/Al₂O₃ have been used for the removal of SO₂ and NO from flue gases and there are also indications that impregnation with metal additives can improve the SO₂ and NO removal performance of activated carbons (Grzybek et. al. 1992). As activated carbon based processes work at lower operating temperatures, adsorption of various reacting gases plays an important role in the overall reaction kinetics. Under this condition, it is of interest to study the adsorption of SO₂ and NO on various adsorbents in order to develop a better understanding of the effects of the adsorbents' physical characteristics on the adsorption characteristics.

The design and simulation of an adsorber and reactor unit for the removal of SO₂ and NO by any process requires a model that accurately describes the process. At the moment, no model is available specifically for the removal of either SO₂ or NO or both from flue gases using activated carbon or impregnated activated carbon. In the literature, the modeling and simulation of various adsorption systems are well documented for various adsorbent and adsorbate systems. However, as removal of NO by carbon based adsorbents is not purely adsorptive, these kinds of models are of little importance. In general, kinetics determined under steady state conditions, as is usually done in Langmuir-Hinshelwood-Hougen-Watson (LHHW) modeling of reaction systems, are not adequate for describing the dynamic behavior of catalytic reactions. In order to construct useful kinetic models, experiments need to be performed under unsteady state conditions. However, no such model to describe dynamic behavior of the NO removal process over activated carbon adsorbents has been reported.
1.3 Research objectives

The main objectives of this research were (1) development of an effective and efficient activated carbon based adsorbent starting from Saskatchewan lignite, (2) development of a process that can effectively remove SO₂ and NO in the presence of O₂ without using a reductant, (3) documenting the adsorption characteristics of SO₂ and NO on lignite and other lignite-derived adsorbents and (4) development of kinetic models for both SO₂ and NO removal from flue gases using lignite adsorbents. Within these overall objectives, various phases of the research were mapped out with each phase having set objectives to accomplish the overall goal of the project. These were:

Phase 1: Preliminary phase

This phase involved:

(a) The design and construction of an experimental rig for adsorption studies.

(b) The design and construction of an experimental rig for carbonization and activation of lignite.

(c) The performing of preliminary experiments in order to establish operating conditions for the characterization of adsorbents.

(d) The performing of preliminary chromatographic experiments in order to determine the optimum analysis conditions and chromatographic columns for SO₂ and NO analysis.

Phase 2: Preparation of char and activated carbon from lignite and their characterization

This phase involved the following:

(a) The evaluation of adsorption characteristics and pore characteristics of the raw material, lignite.

(b) The carbonization and activation of lignite to produce char and activated carbon,
respectively.

(c) The evaluation of the gaseous products produced during carbonization.

(d) The determination and comparison of adsorption characteristics and pore characteristics of char and activated carbon with that of lignite.

(e) The optimization of the carbonization and activation process parameters on the basis of pore characteristics and adsorption characteristics.

Phase 3: Preparation and characterization of impregnated activated carbons

The following were done in this phase of the project:

(a) The preparation of metal-impregnated activated carbon adsorbents.

(b) The characterization of metal-impregnated activated carbon adsorbents.

(c) The elucidation of the processes taking place during adsorbent calcination.

Phase 4: Adsorptive and reactive removal of SO₂

This phase of the project involved:

(a) The evaluation of SO₂ removal performances of various metal-impregnated activated carbon adsorbents.

(b) The study of the effect of the presence of oxygen on the SO₂ removal performance of various adsorbents.

(c) The study of the effect of the valence state of the impregnated metal species.

(d) A comparison of the above results with the performance of the best adsorbent from phase 2.

Phase 5: Adsorptive and reactive removal of NO by lignite and various other lignite-derived adsorbents

The following were done in this phase of the project:

(a) The evaluation of NO removal performances of lignite, char and activated carbon.
(b) The evaluation of NO removal performance of metal impregnated activated carbon adsorbents.

(c) A study of the effect of the presence of oxygen on the NO removal performance of various adsorbents.

(d) A study of the effect of the valence state of the impregnated active metal species.

(e) A comparison of these results with the performance of the unimpregnated activated carbon adsorbent.

Phase 6: Simultaneous removal of SO₂ and NO

This phase involved the following:

(a) A study of the simultaneous removal of SO₂ and NO.

(b) A comparison of the multicomponent adsorption characteristics with single component adsorption characteristics of the metal-impregnated activated carbon.

(c) A study of the effect of the presence of oxygen on the simultaneous removal of SO₂ and NO by metal-impregnated activated carbons.

Phase 7: Modeling and simulation of SO₂ adsorption and NO reaction

This phase was designed to:

(a) Develop a model for the prediction of SO₂ breakthrough profile on activated carbon.

(b) Perform a comparison of the predicted breakthrough profile with the experimental breakthrough profile.

(c) Develop a reaction mechanism for NO removal.

(d) Develop a rate equation for NO removal using unsteady state approach and then estimate the kinetic parameters.
Phase 8: Catalytic reduction of NO by in-situ decomposition and steam reforming of methanol

This phase involved:

(a) A study of the effect of methanol concentration on the reducibility of nitric oxide.
(b) A study of the effect of temperature on the non-selective reduction of nitric oxide.
(c) A study of the effect of presence of oxygen on the reduction of nitric oxide.
2. Literature Review

2.1 Introduction

This chapter presents a review of the existing SO\textsubscript{2} and NO\textsubscript{x} removal technologies. Emphasis is placed on the SO\textsubscript{2} and NO\textsubscript{x} removal characteristics of various adsorbents, their preparation and characterization as well as the modeling of both the SO\textsubscript{2} and NO\textsubscript{x} removal processes.

2.2 Formation of nitric oxides and sulfur dioxide

Nitric oxides (NO\textsubscript{x}) is a generic name given to oxides of nitrogen (N\textsubscript{2}). The major oxides of nitrogen are NO and NO\textsubscript{2} with NO constituting over 90-95 vol\% (Bosch and Janssen, 1987). SO\textsubscript{2} is the chemical formula for sulfur dioxide. This section deals with the formation of NO and SO\textsubscript{2}.

The major source of NO\textsubscript{x} is the burning of fossil fuels at high temperatures in power generating devices such as electric power plants, and automobile exhausts. According to the literature, the contribution of NO\textsubscript{x} from the burning of the fossil fuels (stationary source) is 28.5 to 44 % (Soderlund and Svensson, 1975; Bottger et. al., 1978). For industrialized countries mobile sources such as automobile exhausts contribute to 45-60% of the total NO\textsubscript{x} emission (van den Kerkhof, 1986; Lange, 1985 and Laulainen, 1982).

Three types of NO\textsubscript{x} can be distinguished in flue gases (Bosch and Janssen, 1987). These are thermal NO\textsubscript{x}, fuel NO\textsubscript{x} and prompt NO\textsubscript{x}. According to Zeldovich (1946) thermal NO\textsubscript{x} is formed by fixation of atmospheric nitrogen with oxygen according to the following mechanism:

\[
\begin{align*}
O_2 + 2 N_2 &= 2 NO + N_2 \quad (2.1) \\
N_2 + 2 O_2 &= 2 NO + O_2 \quad (2.2)
\end{align*}
\]
The fixation process is sensitive to temperature (Glick et. al., 1957). For example, in cool (low temperature) flames, the formation of thermal NO\textsubscript{x} is low whereas in high temperature flames, formation of thermal NO\textsubscript{x} is high. In addition to this mechanism, Lavoie et. al. (1970) and de Soete (1981) have indicated that the following reaction can occur in fuel-rich flames:

\[ \text{N}_2 + 2 \text{OH}^{-} = 2 \text{NO} + 2 \text{H} \]  \hspace{1cm} (2.3)

Unlike the formation of thermal NO\textsubscript{x}, fuel NO\textsubscript{x} is formed by the oxidation of the nitrogen containing compounds in the fuel. This process is independent of the temperature of the flame. According to the Fenimore mechanism (Fenimore, 1972), the organic nitrogen compounds, present in coal, form a complex with N\textsubscript{2} which is subsequently attacked by OH radicals and NO molecules as follows:

\[ \text{N-complex} + \text{OH}^{-} = \text{NO} + \text{other products} \]  \hspace{1cm} (2.4)
\[ \text{N-complex} + \text{NO} = \text{N}_2 + \text{other products} \]  \hspace{1cm} (2.5)

Prompt NO\textsubscript{x} is produced by a mechanism that involves the formation of intermediate HCN (due to the reaction of nitrogen radicals and hydrocarbons), and its subsequent to NO. Unlike in the case of thermal and fuel NO\textsubscript{x}, the formation of prompt NO\textsubscript{x} has a weak temperature dependence and, thus, is only significant in very fuel-rich flames (Fenimore, 1971; Hayhurst and McLean, 1974).

The individual contributions of these processes to the overall NO\textsubscript{x} formation is dependent on factors such as the oxygen partial pressure, combustion temperature, fuel type, fuel to air ratio, and residence time for combustion.

The oxides of nitrogen play a major role in the photochemistry of both the troposphere and stratosphere. NO\textsubscript{x} contributes to photochemical air pollution by facilitating ozone formation (Cox and Penkett, 1983).

SO\textsubscript{2} is formed by the oxidation of the sulfur compounds present in the fuel as follows:
\[ RSH + O_2 = SO_2 + RH \] (2.6)

Both \( NO_x \) and \( SO_2 \) contribute to the formation of acid rain (Cox and Penkett, 1983).

2.3 Control technologies for nitric oxides

The initial type of measures introduced in Japan, USA and Germany in the early 1970s to reduce \( NO_x \) emission was based on combustion. At the present time, emission standards have become increasingly stringent. Consequently, simple combustion methods are no longer adequate. Increasingly stringent emission standards have led to more advanced combustion technology and the introduction of additional flue gas treatment. Nowadays, the technological measures used to meet stringent environmental legislation as it applies to emissions in the atmosphere, include either measures during combustion (primary methods or clean techniques), or cleaning of the flue gases (secondary methods or clean-up techniques or flue gas treatments), or a combination of both.

Primary measures include selection of a fuel with low nitrogen content, the design of an efficient burner system to minimize the formation of \( NO_x \) or the addition of more oxygen to the fuel. Details of these primary measures are available in OECD publications (1983). Emission control of \( NO_x \) in coal combustion has been reviewed recently by Reh (1986).

As previously mentioned, secondary measures are those which are applied to clean \( NO_x \) after they are formed. Secondary measures can be categorized into wet and dry processes. This classification is shown in detail in Figure 2.1.
Figure 2.1  Available Techniques to Decrease Emission of Nitric Oxide
2.3.1 Wet processes

Wet processes for the removal of NO\textsubscript{x} are based primarily on the principle of absorption. As shown in Figure 2.1, there are two types of wet NO\textsubscript{x} removal processes. These are direct absorption process and the oxidation absorption process.

Direct absorption process

Two examples of the direct absorption process reported in the open literature (OECD report, 1983) are the sodium acetate process and the complex salt absorption process.

The sodium acetate process basically involves two reaction stages. These are absorption and formation of gypsum stage, and imide treatment stage.

Absorption and formation of gypsum (SO\textsubscript{2}, NO absorption step)

Absorption:

\[
\text{SO}_2 + 2\text{CH}_3\text{COONa} + \text{H}_2\text{O} = \text{Na}_2\text{SO}_3 + 2\text{CH}_3\text{COOH} \tag{2.7}
\]

\[
2\text{NO} + 5\text{Na}_2\text{SO}_3 + 4\text{CH}_3\text{COOH} = 2\text{NH(}\text{NaSO}_3\text{)}_2 + \text{Na}_2\text{SO}_4 + 4\text{CH}_3\text{COONa} + \text{H}_2 \tag{2.8}
\]

Gypsum formation:

\[
\text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{CH}_3\text{COOH} = \text{CaSO}_4\cdot 2\text{H}_2\text{O} + 2\text{CH}_3\text{COONa} \tag{2.9}
\]

Imide treatment process

Hydrolysis:

\[
\text{NH(}\text{NaSO}_3\text{)}_2 + 2\text{H}_2\text{O} = \text{NH}_4\text{HSO}_4 + \text{Na}_2\text{SO}_4 \tag{2.10}
\]

Release of NH\textsubscript{3}:

\[
\text{NH}_4\text{HSO}_4 + \text{Ca(OH)}_2 = \text{NH}_3 + \text{CaSO}_4\cdot 2\text{H}_2\text{O} \tag{2.11}
\]

Nitrogen gas formation:

\[
4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O} \tag{2.12}
\]
According to an OECD report (1983), a large ratio of absorption liquid/flue gas is necessary in commercial applications. This requires a relatively large absorption tower.

In the complex salt absorption process, NO is directly absorbed and fixed as a complex, and then subsequently decomposed into N₂ and O₂. The complex can also be treated to release concentrated NO or fixed as ammonium sulfate. The complex salt absorption process has the advantage that the disposal of the waste solution is relatively simple because no nitrate is left in the absorption solution. For the formation of the complex compounds by absorbing NO, Fe(II) and Fe(III) must be chelated beforehand, to which Na₂SO₃ and (NiI)₂SO₃ are added. The chelating agents can be EDTA, citric acid or oxalic acid, for example (Suzuki et al., 1980). The presence of oxygen in the system reduces the denitrification efficiency of the complex salt absorption process.

Oxidation absorption process

The oxidation absorption process involves the initial oxidation of NO to NO₂ by oxidizing agents such as O₃ or ClO₂ and then subsequent absorption of the NO₂ in an aqueous solution of NaOH or Ca(OH)₂. According to Suzuki et al. (1980) and OECD report, (1983) the oxidation process using O₃ rather than ClO₂ as the oxidizing agent is preferred because of the simplicity of the operation. Ca(OH)₂ is usually used as the absorbent because it is more economical than NaOH. A liquid phase oxidation method using KMnO₄ has also been investigated (OECD report, 1983).

2.3.2 Dry processes

These are processes that do not involve the use of liquid adsorbents. They are based on either the direct reduction of NOₓ to N₂ and other harmless products, adsorptive removal of NOₓ by adsorbents such as activated carbons (Richter, 1985), or decomposition of NOₓ by thermal irradiation (Suzuki et al., 1980; Matsuda et al., 1981; Tokunga and Suzuki, 1984). Of these three types of dry processes, it has been shown that the processes based on direct reduction are more effective and efficient
compared to the other two categories. When compared to the wet process, the dry reduction based process is simple, requires less space, generates no troublesome by-products and requires no tail-gas reheating. These reduction processes can be classified as non-selective non-catalytic reduction, selective non-catalytic reduction, non-selective catalytic reduction, selective catalytic reduction. This review will focus on the selective catalytic reduction (SCR) process since it is considered to be the best NO$_x$ removal technology (Bosch and Janssen, 1987).

Selective catalytic reduction (SCR)

This process involves the selective catalytic reduction (SCR) of NO$_x$ with reductants such as NH$_3$, CH$_4$, H$_2$, CO, C$_x$H$_y$ in the presence of O$_2$ over a catalyst. It is desirable that the process is selective for NO$_x$ reduction alone in the presence of O$_2$ since O$_2$ is always present where NO$_x$ is produced.

SCR using ammonia as the reductant

In this method, ammonia (NH$_3$) is injected into the flue gas stream. This NH$_3$ in the presence of O$_2$ reduces the NO$_x$ in the flue gas over a catalyst such as V$_2$O$_5$/TiO$_2$ at temperatures ranging from 573 to 673 K. NH$_3$ has been found to be a very selective reducing agent (Richter, 1990; Otto et.al., 1970). The overall reactions involved are:

\[
4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 = 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (2.13)
\]
\[
6 \text{NO}_2 + 8 \text{NH}_3 = 7 \text{N}_2 + 12 \text{H}_2\text{O} \quad (2.14)
\]

SCR units can be retrofitted in an existing power plant in three positions which are termed as high-dust, low-dust and tail end system (Janssen, 1993). In the high-dust system the SCR catalyst is placed between the economizer and the air preheater. With this arrangement the flue gas still contains fly-ash and sulfur oxides. The presence of these materials can cause serious degradation of the SCR catalyst, principally due to a side reaction involving the oxidation of SO$_2$ into SO$_3$. SO$_x$ and
wet flue gas may react forming sulfuric acid, which may be a cause of catalyst
deterioration, damage downstream equipment and result in the emission of acidic
particles and aerosols. These particles contain Fe, Ca and sulfates (Gutberlet, 1990).
Vanadium is a catalyst which promotes the formation of SO₃. At lower temperatures
(350°C) the catalyst chemisorbs H₂SO₄ whereas at higher temperatures H₂SO₄
desorbs.

In the low-dust system the SCR reactor is situated downstream of the
electrostatic precipitator (ESP), but before the air preheater. This means that flue
gases reaching the SCR catalyst are almost dust-free, however the gas stream still
contains SO₂. A major problem in low-dust systems SCR is coverage of the catalyst
pores by very fine dust particles which escape precipitation in the ESP, thus making
the catalyst surface becomes unavailable for catalytic action.

Tail-end systems are situated at the end of the flue gas treatment plant. At
this point flue gas contain only a small amount of SO₂ and particles. As catalytic
removal of NOₓ requires high temperature (350-450°C) preheating of the flue gas is
an essential feature in tail end systems.

The reactor configuration as well as the geometry and composition of the
catalyst used for the SCR of NOₓ are strongly dependent on the location of the SCR
unit within the power plant. This is because the location of the SCR unit determines
the properties of the flue gas from which NOₓ is to be removed as mentioned
previously.

More than a thousand catalyst compositions have been tested for application
for the selective catalytic reduction of NOₓ. These are: noble metals such as Pt on
Al₂O₃ or SiO₂, vanadia material such as V₂O₅ on TiO₂ (Wong and Nobe, 1986) or on
SiO₂ (Odenbrand et. al., 1985) or on Al₂O₃ (Nam et. al. 1986), V₂O₅/WO₃ on TiO₂
(Janssen et. al., 1985), WO₃ on TiO₂, iron such as Fe₂O₃ on TiO₂ or on Cr₂O₃/Al₂O₃,
copper oxides such as CuO on TiO₂ or on Al₂O₃ (Canti et. al., 1990). Zeolites are
also employed at the high temperature end of the SCR process spectrum. Zeolite-
based catalysts can be impregnated with base metals (Byrne et. al., 1990) such as iron
or copper to increase the catalytic activity at low temperatures. The zeolite
components can be clinoptilolite (Gerdes et. al., 1988), ZSM-5 (Krishnamurthy et. al., 1988), mordenite (Medros et. al., 1989) or zeolite beta (Byrne et. al., 1990).

Activated carbon has been used to reduce nitric oxide or catalyze its reduction in the SCR with ammonia process (Richter, 1985). In this process, it is well known that the carbon is ultimately consumed. However, it has been reported that a large facility for the SCR of NO\textsubscript{x} is in operation in Germany (Richter, 1990). A thorough review of the SCR process and various catalyst systems has been published by Bosch and Janssen (1987).

The major problems associated with the SCR of NO\textsubscript{x} using ammonia as the reductant are NH\textsubscript{3} slip, an expensive auxiliary NH\textsubscript{3} distribution system, NH\textsubscript{3} storage, flue gas reheating and the high operating temperature of the SCR catalyst. A brief review of these problems is given below in order to justify the importance of trying other reductants. There are several problems that limit the application of the SCR process.

In order to achieve 80% removal of NO\textsubscript{x} from the influent stream, ammonia is injected into the flue gas prior to the catalyst. This requires a sophisticated distribution system of pipes and nozzles. A large amount of NH\textsubscript{3} added for the NO\textsubscript{x} reduction means that anhydrous ammonia will remain unreacted. This constitutes NH\textsubscript{3} slip, which is usually vented to the atmosphere. Thus, the process generates another pollutant (ca. 5-10 ppm NH\textsubscript{3}).

If the flue gas contains SO\textsubscript{2}, when NH\textsubscript{3} is added as the reductant, ammonium sulfates form at temperatures below 350°C. This is known to cause the coating of the downstream process equipment (Armor, 1992); this essentially implies that high temperature operation is needed. On the other hand, if the SCR unit is placed in the high dust system to take advantage of the high operating temperature, there is the problem of high dust and high SO\textsubscript{2} which results in catalyst deactivation. Therefore, the optimum operation of the SCR unit is as an add-on unit in the tail end position. However, operation of the SCR unit in this position requires an extreme flue gas reheating which makes the process very expensive.
SCR using other reductants

To avoid the problems associated with the use of NH\textsubscript{3}, extensive research work has been carried out and the use of metal containing zeolites and supported copper catalysts for removing NO\textsubscript{x} in auto-exhausts has been proposed. Two exciting research developments are associated with zeolite-based denitrogenation (DeNO\textsubscript{x}) catalysts. The early research development relates to the decomposition of NO\textsubscript{x} to N\textsubscript{2} and O\textsubscript{2}. This reaction is heavily favored by thermodynamics at typical exhaust gas temperatures. Noble metal catalysts are active but strongly inhibited by oxygen (Amirnazmi and Boudart, 1975), and base metal oxide catalysts exhibit activities that are too low to be of use. Recent work with Cu-ZSM-5 (Iwamoto et. al., 1990; Iwamoto, 1990 and Li and Hall, 1991) for the decomposition of nitric oxide has led to a variety of other catalysts for the reduction of nitric oxide by C\textsubscript{2} hydrocarbons.

Hamada et. al. (1990) has observed that H-forms of a number of zeolites catalysts are particularly effective for the reduction of NO\textsubscript{x} by C\textsubscript{3}H\textsubscript{8} at 300°C in the presence of 10% oxygen. These authors indicated that the use of propene enabled the temperature to be reduced to 200°C with carbon dioxide formed as the only byproduct. It was also shown that oxygen is essential for the reaction. Iwamoto et. al. (1991) also reported the selective catalytic reduction of NO\textsubscript{x} by C\textsubscript{4}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, C\textsubscript{4}H\textsubscript{8} and C\textsubscript{3}H\textsubscript{8} in the presence of oxygen. SO\textsubscript{2} showed only a slight adverse effect on the performance of the catalyst. An SCR process has been developed by Li and Armor (1992) which uses CH\textsubscript{4} as the reducing agent over Co-ZSM-5 catalyst.

Although extensive research is being carried out on the possible use of the hydrocarbons for commercial SCR of nitric oxide, NH\textsubscript{3} continues to be the dominant reductant for the SCR of NO\textsubscript{x}.

2.4 Control technologies for sulfur oxides

SO\textsubscript{x} or sulfur oxides is a generic term used to represent both sulfur dioxide (SO\textsubscript{2}) and sulfur trioxide (SO\textsubscript{3}). It is well known that a large portion of SO\textsubscript{x} is made up of SO\textsubscript{2} (>95%). Consequently, attention is usually focused on the removal of SO\textsubscript{2}. Various methods for the removal of SO\textsubscript{2} are non-regenerative alkaline processes,
regenerative alkaline processes, furnace injection processes, regenerative organic absorption processes, catalytic processes and regenerative solid adsorption processes (Davis, 1972). A review of these methods is presented below.

2.4.1 Non-regenerative alkaline Processes:

This category of process is considered to be throwaway processes. In this process such as CaO an agent combines chemically with SO₂ in the flue gas stream according to the reaction (Armor, 1992).

\[
\text{CaO + SO}_2 + \text{O}_2 + \text{H}_2\text{O} = \text{CaSO}_4 \cdot 5\text{H}_2\text{O}
\]  

(2.15)

In this case, the SO₂ reactants are so cheap that it is more economical to throw away the sulfated product (e.g., gypsum) than to attempt a regeneration of the starting material and, thus, it is used on a once-through basis. Commonly used agents are limestone lime, dolomite and the solid carbide wastes from acetylene manufacturing.

Reliable methods of contacting SOₓ in flue gas with the limestone (CaCO₃) are by wet limestone scrubbing and limestone injection; this is a non-catalytic process and is described briefly below.

In the wet-limestone flue gas desulfurization (FGD) system the flue gas is first passed through an ESP (electrostatic precipitator) to remove fly ash, and then absorbed on a slurry of wet limestone where it reacts with the limestone to form CaSO₃·5H₂O. The latter is eventually oxidized in the presence of O₂ (also present in the flue gas) to form gypsum, CaSO₄·2H₂O, which can then be recovered and disposed of either as a wet sludge or as a dry, bagged product.

In the lime (CaO) spray-drying process flue gas is contacted with a finely atomized Ca(OH)₂ slurry. Complete evaporation of water in the product occurs to produce a dry powder (CaSO₄). This dry solid product together with the fly ash is separated by an ESP from clean flue gas and routed for disposal or recycle. Lime
spray-drying is less efficient and more expensive than wet limestone scrubbing. Hence, it is generally used for the FGD of low sulfur coal or in small facilities. According to Davis (1972), the major problem with this approach is finding a use for the by-product CaSO\(_4\) which is usually produced in huge quantities. The use of this product for wallboard, and in landfills has been reported (Armor, 1992). The Claus process represents an alternative way to remove SO\(_2\) according to the reaction:

\[ 2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O} \]  

(2.16)

This process also produces a by-product, sulfur, and requires the use and handling of H\(_2\)S. US refineries are now a major source of elemental sulfur. However, sulfur also does not command much market value. Therefore, processes have been suggested where SO\(_2\) is converted to a more useful product such as sulfuric acid.

### 2.4.2 Regenerative alkaline processes

In the regenerative alkaline process, an alkaline agent (for example, sodium sulfite (Na\(_2\)SO\(_3\))) is used to strip SO\(_2\) from the flue-gas stream by combining with SO\(_2\) chemically. The major product from this process is sodium bisulfite (NaHSO\(_3\)). Subsequently, the sodium sulfite is regenerated and the sulfur dioxide is recovered as shown in Equation 2.18. Usually, the sulfur (S), stored in SO\(_2\), is recovered either as liquid S or sulfuric acid.

\[ \text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} = 2\text{NaHSO}_3 \]  

(2.17)

\[ 2\text{NaHSO}_3 = \text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \]  

(2.18)

One of the commercial processes based on this approach is the Wellman-Lord process. This process is based upon the absorption of SO\(_2\) by an aqueous solution of Na\(_2\)SO\(_3\) to produce NaHSO\(_3\). The resulting solution of NaHSO\(_3\) is heated to generate a stream of SO\(_2\) which usually is catalytically reduced to sulfur by H\(_2\)S or methane (CH\(_4\)). These are given in equations 2.19 - 2.22.
\[
\begin{align*}
\text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} &= 2\text{NaHSO}_3 \quad (2.19) \\
2\text{NaHSO}_3 &= \text{Na}_2\text{SO}_3 + \text{SO}_2 + \text{H}_2\text{O} \quad (2.20) \\
\text{CH}_4 + 2\text{SO}_2 &= \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{S} \quad (2.21a) \\
4\text{CH}_4 + 6\text{SO}_2 &= 4\text{CO}_2 + 4\text{H}_2\text{O} + 4\text{H}_2\text{S} + 2\text{S} \quad (2.21b) \\
\text{Claus reaction: } 2\text{H}_2\text{S} + \text{SO}_2 &= 2\text{H}_2\text{O} + 3\text{S} \quad (2.22)
\end{align*}
\]

2.4.3 Furnace injection process

As in the non-regenerative alkaline process, the furnace injection method is also a throwaway process. However, it differs from the former in that in the latter case, the agent is injected directly into the furnace and the sulfated product is subsequently scrubbed out of the flue gas with water.

2.4.4 Regenerative organic absorption process

The regenerative organic absorption process is essentially similar to the regenerative alkaline process. However, it differ from the latter in that an organic absorbing medium is used in the absorption step.

2.4.5 Catalytic processes

In these processes, a catalyst is used to promote the oxidation of SO\textsubscript{2} to SO\textsubscript{3} which reacts with water present in the flue gas to produce sulfuric acid. To avoid chemisorption of sulfuric acid on the catalyst a high inlet-gas temperature is required. Armor (1992) has carried out a brief review of the oxidation processes of practical importance. These are described briefly as follows.

In one of the oxidation processes proposed and tested in Monsanto (Cat-Ox process), SO\textsubscript{2} from the ESP unit is oxidized over a V\textsubscript{2}O\textsubscript{5} catalyst to produce SO\textsubscript{3} which is then treated with water to form H\textsubscript{2}SO\textsubscript{4}. This Cat-Ox process is not attractive because it is characterized by high operating costs.

Another oxidation process is the Haldor Topsoe SNO\textsubscript{x} process. In this case, a V\textsubscript{2}O\textsubscript{5} based catalyst is used to oxidize dilute SO\textsubscript{2} to produce H\textsubscript{2}SO\textsubscript{4}. Another oxidation based process is the DeSO\textsubscript{x} process developed by Atlantic Richfield.
Company. In this process, uses cerium containing spinels (CeO$_2$/nMgO$_2$MgAl$_2$O$_4$) are used to control SO$_x$ emissions from fluid catalytic cracking (FCC) regenerators as reported by Armor (1992). The CeO$_2$ serves as an oxidation catalyst for the reaction which is represented by the following scheme.

\[
\begin{align*}
\text{SO}_2 + \frac{1}{2}\text{O}_2 &= \text{SO}_3 \\
\text{SO}_3 + \text{MgO (s)} &= \text{MgSO}_4 (s) \\
\text{MgSO}_4 (s) + \text{H}_2 &= \text{MgO (s)} + \text{H}_2\text{S} + \text{H}_2\text{O}
\end{align*}
\]

(2.23) (2.24) (2.25)

The alumina of the spinel serves to enhance the hydrogen reduction of the sulfate to produce H$_2$S.

2.4.6 Regenerative solid adsorption processes

This category comprises several activated char processes in which SO$_2$ is adsorbed in the presence of H$_2$O and O$_2$ (both from the flue gas) as H$_2$SO$_4$ on char. In the subsequent desorption step, SO$_2$ is desorbed by thermal decomposition of sulfuric acid.

2.5 Simultaneous removal of sulfur dioxide and nitric oxides

Usually the fuel used for power generation contains sulfur compounds. Consequently, SO$_2$ will be present in the flue gas alongside NO$_x$. With the increasing environmental restrictions on the emissions of SO$_2$ and NO$_x$ worldwide, it appears that the technologies mentioned earlier in Sections 2.2 and 2.3 for NO$_x$ and SO$_2$ removal, respectively, will be incapable of accomplishing these NO$_x$ and SO$_2$ limits. According to Richter (1990), what is needed is an integrated gas clean-up technology which can simultaneously remove SO$_2$ and NO$_x$. Such processes include NOXSO, SNO$_x$, DeSONO$_x$, CuO/Al$_2$O$_3$ and carbon adsorbent technology. These are described in detail below.
In the literature (Richter, 1990), simultaneous removal of SO\textsubscript{2} and NO\textsubscript{x} includes stagewise removal of both SO\textsubscript{2} and NO\textsubscript{x} from flue gas as well as removal in a one step process. For example, in the two stage process, NO\textsubscript{x} may be removed in the first stage by the SCR process while SO\textsubscript{2} is removed in the second stage by processes such as the DeSO\textsubscript{x} process. An example of the one step process is the copper oxide process. Details are given below.

2.5.1 NOXSO process

The NOXSO process for simultaneous removal of both SO\textsubscript{x} and NO\textsubscript{x} uses a high surface-area alkalized alumina (γ-alumina support impregnated with Na\textsubscript{2}CO\textsubscript{3}). Removal of NO\textsubscript{x} and SO\textsubscript{2} from flue gas with alkalized alumina sorbent is achieved at 90-150\degree C in a fixed bed of the sorbent. The NO\textsubscript{x} and SO\textsubscript{x} are converted in the fixed bed to NO\textsubscript{3}\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-}, respectively. The spent alkalized alumina is regenerated by treatment with hydrogen and/or methane at 610\degree C to remove SO\textsubscript{2}, H\textsubscript{2}S and sulfur (Richter, 1990). SO\textsubscript{2} and H\textsubscript{2}S can then be converted to elemental sulfur by the Claus process. At the high regeneration temperatures, NO\textsubscript{x} is driven off the catalysts and returned to the boiler with combustion air. Since the reaction of N\textsubscript{2} with O\textsubscript{2} to produce thermal NO\textsubscript{x} is reversible, increasing the concentration of NO\textsubscript{x} in the boiler will lead to a less favorable equilibrium for the formation of NO\textsubscript{x}.

2.5.2 SNO\textsubscript{x} process

The SNO\textsubscript{x} process for the removal of NO\textsubscript{x} and SO\textsubscript{x} uses a combination of the SCR technology for NO\textsubscript{x} removal and the SO\textsubscript{2} oxidation process which converts SO\textsubscript{2} to SO\textsubscript{3} and then to H\textsubscript{2}SO\textsubscript{4}. According to Armor (1990), in the Haldor-Topsoe SNO\textsubscript{x} process, flue gas at 200\degree C is deducted with bag filters and preheated to 380\degree C via a heat exchanger before NO\textsubscript{x} is removed by a conventional SCR technology using ammonia as the reductant over a monolith catalyst (Topsoe DNOX catalyst). The products (essentially N\textsubscript{2} and SO\textsubscript{2}) are heated to 420\degree C where the SO\textsubscript{2} is oxidized to SO\textsubscript{3} gas in a fixed bed containing V\textsubscript{2}O\textsubscript{5} catalyst. The conversion obtained is reported to be about 95%. The gas is then cooled in a gas/gas heat exchanger and then goes
through a wet gas sulfuric acid (WSA) condenser which works as an air-cooled, falling-film condenser. With this air-cooled, falling-film condenser, H$_2$SO$_4$ vapor is condensed to produce 94-97% H$_2$SO$_4$. An SNO$_x$ plant for NO$_x$ and SO$_2$ removal is under construction in Denmark.

2.5.3 DeSONO$_x$ process

The DeSONO$_x$ process is similar to SNO$_x$ except that it uses a zeolite based SCR catalyst for NO$_x$ removal and does not include a falling film evaporator. Also, only about 70% H$_2$SO$_4$ is produced. In the case of the DeSONO$_x$ process, the SCR catalyst used operates at high temperature (ca. 420°C). This obviates the need for a preheater prior to SO$_2$ oxidation. This process is being used in a power plant in Munster, Germany (Richter, 1990).

2.5.4 Copper oxide process

The copper oxide process is an example of the one-step, simultaneous NO$_x$ and SO$_2$ removal process. In this process, a commercial catalyst (UOP SOX-3) consisting of spheres of copper oxide (6.5 wt%) impregnated on γ-alumina is used as an adsorbent/oxidation catalyst for SO$_2$ removal (4900 ppm) (equation 2.26) and as a catalyst for the reduction of NO using ammonia (NH$_3$) as a reductant (equation 2.15).

\[
4 \text{ NO} + 4 \text{ NH}_3 + \text{ O}_2 = 4 \text{ N}_2 + 6\text{H}_2\text{O} \quad (2.15)
\]
\[
\text{CuO} + \text{ SO}_2 + 1/2 \text{ O}_2 = \text{CuSO}_4 \quad (2.26)
\]

The partially sulfated copper sorbent obtained from reaction 2.26 is heated to 450-500°C in a separate fluidized bed operation and regenerated with natural gas as the reductant. Other reductants that can be used include hydrogen (H$_2$) and carbon monoxide (CO).

\[
\text{CuSO}_4 + 1/2 \text{ CH}_4 = \text{Cu} + \text{ SO}_2 + 1/2 \text{ CO}_2 + \text{H}_2\text{O} \quad (2.27)
\]
The regenerated sorbent is cooled and recycled to the adsorber where Cu\(^{\circ}\) is rapidly oxidized by oxygen (O\(_2\)) present in the flue gas (Harriott and Markussen, 1992).

\[
\text{Cu} + \frac{1}{2} \text{O}_2 = \text{CuO} \tag{2.28}
\]

A number of reactor designs have been evaluated. Currently a fluidized bed reactor is undergoing a large scale development testing. In this process, water vapor is known to reduce catalytic activity (Kiel et al., 1992).

2.5.5 Carbon adsorbent technology

As mentioned earlier in Section 2.2 and 2.3, the use of carbon offers an alternative process which could be employed for the simultaneous removal of SO\(_2\) and NO\(_x\) arising from the burning of fossil-fuels. This process appears to be the best method for solving the air pollution problems since it can be used for simultaneous removal of SO\(_2\) and NO\(_x\) at relatively low temperatures. In carbon adsorbent technology, the carbon (adsorbent) acts as both reactant and catalyst. Usually, NO\(_x\) and SO\(_2\) removal is accomplished in a reactor containing two moving beds. Therefore, for a flue gas containing both SO\(_2\) and NO\(_x\), the first moving bed of activated coke sorbs and oxidizes SO\(_2\) to SO\(_3\) and then to H\(_2\)SO\(_4\) (in the presence of H\(_2\)O) at temperatures as low as 20\(^\circ\)C. Also nitrogen dioxide (NO\(_2\)) in the flue gas stream is adsorbed and reduced to NO. CO\(_2\) is also produced in the process. In the second moving bed, NH\(_3\) is added to reduce the NO (formed in the first bed as well as the one present originally in the flue gas) to N\(_2\). In this process, carbon is used as a catalyst. Upon saturation of the first bed of activated coke, the sorbent is regenerated by heating at 650\(^\circ\)C in an inert atmosphere where SO\(_3\) desorbs and is then subsequently reduced to a concentrated stream of SO\(_2\). The SO\(_2\) is further reduced by activated coke at 649\(^\circ\)C. A removal efficiency of 98% SO\(_2\) and 50% NO\(_x\) has been reported by Richter (1990) for this process. However, there are various disadvantages associated with this carbon adsorbent technology process. According
to Armor (1990) the disadvantages of carbon adsorbent technology are: low flue gas velocity, large carbon bed volumes, and loss of carbon by consumption during the process of reaction and regeneration, and the loss of carbon due to attrition.

2.6 Selection of lignite for preparation of activated carbon

Processes such as the BF-Uhde process mentioned in Section 2.5 use activated coke or activated carbons which are derived from sub-bituminous or bituminous coals (high rank coals). However, studies in the literature (Kisamori et al., 1991; Wigmans, T, 1986) suggest that other carbonaceous precursors such as low rank coals, polymeric substances may provide cheaper alternatives for activated carbon manufacture. In this section, a review of the various structures of coal as well as criteria for their selection for the preparation of activated carbon for the adsorptive removal of SO₂ and NOₓ is presented.

2.6.1 Structure of coal

Coal is defined by Wen and Lee (1979) as a complex heterogeneous material which is composed of organic and inorganic constituents. The organic fraction of coal is made of macerals. There are three major group of macerals: vitrinite, liptinite and inertinite. Liptinite macerals have the lowest specific gravity whereas the inertinites have the highest. Liptinites are rich in hydrogen and can be convert into liquid and gaseous fuels more readily than other maceral groups. Vitrinites are next to liptinites in convertibility. Liptinites and vitrinites are the preferred macerals in coking of coals.

Any discussion on the structural characterization of coal must invariably start with the classical X-Ray studies of Cartz and Hirsch (1960), and Hirsch (1954). Cartz and Hirsch examined several vitrains of different rank. X-Ray scattering at high medium and low angles were attributed to small condensed aromatic layers parallel to each other, and to discontinuities in the structure, respectively. Amorphous material in coal also contributes to scattering at high angles. The important conclusions of the X-ray study are summarized below.
Layer size distribution in the vitrains varies in the 0.5-3 nm range. Below 89% carbon, about 14% of the carbon in the vitrain occurs as single layers, and the remainder (apart from the amorphous carbon) occurs in layers stacked parallel to each other in groups of 2,3 etc. The fraction of single layers decreases with increase in rank, and at 94% carbon content, it amounts to only 10%. This implies that the packing of layers improves with rank. The fraction of amorphous material in vitrain decreases linearly from about 38% for a vitrain of ~57% carbon content to about 28% for a vitrain of ~83% carbon content. The fraction of amorphous material decreases sharply thereafter with increasing rank; for a vitrain of 94% carbon content, the fraction of amorphous material is only 10%.

Three types of structures have been distinguished from a study of a wide variety of coals: open, liquid and anthracitic structure.

The open structure is characteristic of low-rank coals with carbon contents up to about 85%. Coals in this range are highly amorphous and the lamellae are connected by cross-links and thus are more or less randomly oriented in all directions.

On the other hand, the liquid structure is characteristic of bituminous coals with carbon contents in the range of 85-91 wt%. In this case, there is a considerable decrease in the number of cross-links. Also, the lamellae show some orientation with the formation of crystallites consisting of two or more of these lamellae.

The anthracitic structure is usually found in higher rank coals with carbon contents above 91 wt%. In this structure, while there is a much higher degree of orientation of the lamellae with regard to each other, there is the disappearance of cross-links resulting in anthracites having smaller pores.

There have been many attempts to determine the chemical structure of coals. These investigations include the studies by van Krevelen (1950), Hill and Lyon (1962), Benjamin et. al. (1978), Elliot (1981) and, Chung and Goldberg (1984).

Figure 2.2 summarizes the proposed chemical structure of coal by Hill and Lyon (1962). Such a model assumes that coal is comprised of large heterocyclic nuclei monomers with alkyl side chains held together by C-C groups. The coal structure also has been shown to contain oxygen functional groups and ether bonds.
Figure 2.2: Typical Cross-Bonded Structure for High Volatile Coals, (Hill and Lyon, 1962), R°N-Alicyclic Rings of N Carbons, RN-Alkyl Side Chain of N Carbons, R'N-Unsaturated Alkyl Side Chain of N carbons, CB-Cross-bonding by O or S to New Heterocyclic Groups With Side Chains, T-Tetrahedral 3-Dimensional C-C, C-O and C-S Bonds
While sulfur and oxygen are present in coal as linking sub-units, nitrogen exists mainly in the heterocyclic ring structures.

2.6.2 Criteria for selection of coal for activated carbon manufacture

As coal is so variable in structure, it is necessary to devise a selection criterion for these coal precursors so that the activated carbon obtained is effective for SO$_2$ and NO$_x$ removal. Takeo et. al. (1986) have reported a selection index applicable to the use of coal as the raw material for producing activated carbon. They have observed that although anthracite has higher fixed carbon and oxygen content, activated carbon prepared from anthracite coal exhibited lower sulfur dioxide removal efficiency compared to the activated carbons prepared from sub-bituminous or bituminous coals. According to these authors, the higher the O/C ratio of the raw carbonaceous material, the higher the SO$_2$ adsorption capacity of the activated carbons derived from such carbonaceous raw materials.

DeJohn (1975) has reported that activated carbon adsorbent prepared from lignite (low rank coal) performed better for waste water pollution control application than those prepared from high rank coals. This result was attributed to the larger pore structure of lignite-derived activated carbon compared with those derived from high rank coals. In addition, it has also been reported (DeJohn, 1975) that it is easier to regenerate lignite-derived activated carbon than bituminous coal-derived activated carbon. However, despite these good characteristics of lignite and lignite-derived activated carbon adsorbent in the removal of SO$_2$ and NO$_x$ from flue gas has not been reported before in the open literature.

2.7 Carbonization and activation of lignite

It is known from the literature that the removal of impurities from gases and vapors by activated carbon is by adsorption. It also is known from the literature that the unique adsorption capacity of activated carbon for gases and vapors is due to its microporous nature. Most of the methods used for increasing the microporosity of carbon adsorbents are but various combinations of two basic operational procedures
(Hassler, 1974). These operational procedures consist of carbonizing the source carbonaceous material under appropriate conditions after which the resulting char is subjected to oxidation in a controlled atmosphere (activation). Carbonization and activation processes will be reviewed in this section.

2.7.1 Selection of carbonization process parameters

Carbonization of coal results in the formation of gas, tar and char. The yields of these products depend on the carbonization temperature, carbonization time, inert gas flow and heating rate. Wen and Dutta (1979) have studied the effect of heating rate and carbonization temperature on the yields of these products. According to these authors, depending on the desired yields, the product distribution, and the processing conditions required, both the heating rates and the temperature zones of carbonization can be classified roughly into four categories, as is shown in Table 2.1 (Wen and Dutta, 1979). Slow heating is the classical procedure that has been practiced for a number of years to make char and cokes. Low, intermediate or high temperatures are used in the carbonization, depending on the desirability of yields of char or volatile matters. As intermediate or high carbonization temperatures result in the production of more liquid and gaseous products, low temperature carbonization is the obvious choice for the preparation of char. Though the effect of various carbonization parameters on the yield of char have been studied in considerable details, very little is reported in the open literature about the optimization of the carbonization process parameters in order to obtain a char with optimum physical characteristics of chars.

2.7.2 Activation of char

The phenomena involved in the char production due to the initial carbonization have been discussed earlier. In most cases, the char produced in the carbonization stage is distinctly different compared to the parent coal in size, shape and pore characteristics. Sometimes the resulting char, which is more porous compared to the parent coal, does not have an adequate improvement in the
Table 2.1: Classification of Carbonization Process on the Basis of Carbonization temperature and Heating Rate As Proposed by Wen and Dutta (1979)

### A. Classification of Heating Rates

<table>
<thead>
<tr>
<th>Heating Rate, °C/s</th>
<th>Heat-up Time to 1000°C for ~ 100 μ in Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Slow heating</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2. Intermediate heating</td>
<td>5 ~ 100</td>
</tr>
<tr>
<td>3. Rapid heating</td>
<td>500 ~ 100,000</td>
</tr>
<tr>
<td>4. Flash heating</td>
<td>&gt; 10⁶</td>
</tr>
</tbody>
</table>

### B. Classification of Temperature Zones for Carbonization of Coal

1. Low temperature carbonization ~ 500°C
2. Intermediate temperature carbonization ~ 750°C
3. High temperature carbonization ~ 1000°C
4. Very high temperature carbonization > 1200°C

### Suggested Temperature Programming Mode

<table>
<thead>
<tr>
<th>Desired Volatile Product</th>
<th>Heating Rate</th>
<th>Temperature of Carbonization</th>
<th>Solid Residence Time</th>
<th>Volatile Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Tar</td>
<td>Rapid</td>
<td>Low (~500°C)</td>
<td>Long</td>
<td>Short</td>
</tr>
<tr>
<td>2. Liquid</td>
<td>Rapid</td>
<td>Intermediate (~750°C)</td>
<td>Long</td>
<td>Long</td>
</tr>
<tr>
<td>3. Gas</td>
<td>Rapid</td>
<td>High (&gt;1000°C)</td>
<td>Long</td>
<td>–</td>
</tr>
<tr>
<td>4. CH₄</td>
<td>Rapid</td>
<td>~600°C</td>
<td>Long</td>
<td>–</td>
</tr>
<tr>
<td>5. H₂</td>
<td>Rapid</td>
<td>1000~1100°C</td>
<td>Long</td>
<td>–</td>
</tr>
<tr>
<td>6. C₃H₂ + unsaturates</td>
<td>Flash</td>
<td>&gt;1200°C</td>
<td>Long</td>
<td>Intermediate</td>
</tr>
<tr>
<td>7. CO</td>
<td>–</td>
<td>Intermediate (~750°C)</td>
<td>Long</td>
<td>–</td>
</tr>
</tbody>
</table>

* Dash means that the effect is either uncertain or insignificant.
adsorption characteristics. As a result, chars are generally subjected to another process which is termed activation. Many of the activation processes involve a reaction with oxidizing gases. The char takes part in second stage char-gas reactions, namely, the char-H₂, char-O₂, char-H₂O and char-CO₂ reactions.

The char-gas reactions that take place during the second stage following the carbonization reaction may be classified into two distinct categories, namely, volumetric reactions and surface reactions. Char-gas reactions, whether of the volumetric or surface type, take place on the external or internal surface of the char. Generally speaking, in the case of char-O₂ and char-H₂ reactions, the surface chemical reaction is very fast and diffusion is the rate controlling step. Volumetric reactions (for example the char-CO₂ and the char-H₂O reactions), on the other hand, are characteristic of slow reactions in porous solids. In the case of volumetric reactions, when a gaseous species reacts with char, the species must diffuse to and be adsorbed on the reactive sites of the char surface before the reaction takes place and the products are formed on the carbon surface. The products must subsequently desorb from the active sites and diffuse out of the particles. In the case of surface reactions, the rate is proportional to the surface area of the reaction surface. For activation of many types of chars, steam is preferable to carbon dioxide and much better than air (Hassler, 1974).

Khan (1987) studied the reactivity of low-temperature chars in relation to their activation. In this study, the reactivity of chars prepared under mild (low-temperature) conditions has been addressed. The chars prepared by mild carbonization of coal at 500°C are shown be highly reactive in subsequent activation reactions. Comparison of reactivities of low and high temperature chars shows that the low temperature chars exhibit higher reactivity than both the parent coals and high temperature chars.

2.7.3 Metal-impregnated activated carbons

It has already been mentioned that SO₂ and NOₓ, formed during combustion of fossil-fuels, can be removed successfully using activated carbon adsorbents at low
temperatures. This technology has drawn attention because in the case of SCR of NO\textsubscript{x} at low temperature, activated carbon catalyst is preferable in those cases where the SCR unit has to be placed as an add-on unit at the end of the flue gas system where temperatures are below 473 K. This offers both practical and economical advantages. In the past, little research on low temperature SCR catalysts has been performed (Singoredjo et. al., 1990). Several metal halide catalysts on different catalyst supports have been compared by Nishijima et. al. (1979) and from this research, carbon supported catalysts turned out to be more active than silica and alumina supported SCR catalysts in the low temperature region. Alumina supported metal halide catalysts have been used by Todo et. al. (1976), while carbon supported copper oxide catalysts were employed by Nozaki et. al. (1977). Recently, Kasaoka et. al. (1989) reported results on both activated carbon and titania/carbon supported vanadium oxides. The catalytic activity of carbon supported copper salts for the selective catalytic reduction of NO was studied by Singoredjo et. al. (1990) in order to develop catalysts, active at temperatures below 473 K. At equal copper to carbon loading and a space velocity of 60,000 h\textsuperscript{-1}, the activity order was CuO>CuBr\textsubscript{2} ≈ CuSO\textsubscript{4}>CuCl\textsubscript{2}. The carbon support showed only a low activity. In the lower temperature region (<473 K), CuO was even more active than titania supported vanadia and vanadia/tungsten oxide catalysts which are known in the published literature to be the best SCR catalysts. These authors reported the presence of a maximum activity point which was explained by both a change in selectivity and in the structure of the catalysts. The CuO/C and the CuBr\textsubscript{2}/C exhibited a constant activity at 423 K for 110 h.

In a study by Klinik and Grzybek (1990), V\textsubscript{2}O\textsubscript{3} supported on activated carbon has been found to be very good catalyst for the removal of SO\textsubscript{2}. These authors also have studied KMnO\textsubscript{4} and Fe\textsubscript{2}O\textsubscript{3} catalysts supported on activated carbon for SO\textsubscript{2} removal.
2.8 Physical characterization of coal and coal-derived microporous adsorbents

As this work involved the development of adsorbents with the "right" physical characteristics from Saskatchewan lignite, the following section will be focused on the physical characterization of coal and coal-derived adsorbents.

2.8.1 Characterization of lignite and lignite-derived adsorbents

It is well known that the pores in coal vary in size from large cracks of micron dimensions to apertures which are even close to the helium molecule size at room temperature. It is the empty volume (known as the pore volume) within the pores of any material that enables it to adsorb large amounts of gases or liquids. A large pore volume does not always imply a large pore surface area because the latter is dependent upon pore size distribution. A large fraction of pores with small dimensions implies a large surface area.

A low grade coal such as lignite is mostly amorphous. On the other hand, a high grade coal such as anthracite is crystalline. Estimation of pore volume, surface area and pore size distribution is therefore necessary for the complete characterization of coal. A review of the techniques available in the literature for the estimation of the physical characteristics are given below.

2.8.1.1 Techniques available for determining microstructure of coal

The microstructure of any material provides information concerning its micropore surface area, volume, pore size and pore size distribution. Knowledge of the microstructure of porous adsorbents and catalysts is of decisive importance as far as the adsorption of gases and vapors is concerned, since material and thermal transport often play an important role above and beyond that of the surface reaction itself. Equally as important in the development and characterization of adsorbents and catalysts is the determination of the surface available for the adsorption and reaction in question.
In a porous solid, the internal surface, i.e., within the pores, provides the largest available surface area; the external surface area of the particle is usually negligible in comparison (Mahajan, 1984). The internal surface area is inversely proportional to the pore size, reaching in excess of 1,500 m²/g with very fine pored materials like zeolites and activated carbons; external surface area is little more than 3-5 m²/g for very fine particles (~1 μm in diameter). To be able to predict whether or not diffusion through the pores (Knudsen diffusion) is likely to have an inhibiting effect on transport in a reaction, it is also necessary to know the relative frequencies of the various pore sizes in the solid, i.e., the pore size distribution.

A comprehensive review of the principal methods for the physical characterization of the microstructure of solids has been published by Seifort and Emig (1991). These methods include:

1. Electron microscopy,
2. X-ray diffraction,
3. Immersion calorimetry,
4. Liquid chromatography,
5. Chemisorption of gases or vapors (NH₃, H₂O) on the solid,
6. Physisorption of gases and liquids (N₂, Ar, Kr, CO₂, C₆H₆) and
7. High pressure mercury-penetration (Hg porosimetry).

Even though all these techniques are available for physical characterization of the microstructure of solids, it appears that the physical adsorption technique has advantages over the other methods. Consequently, it has become the most widely used technique (Seifort and Emig, 1991).

2.8.1.2 Physical adsorption technique for determining microstructure

The basis of all physisorption studies of the microstructure is sorption isotherm data, which is obtained from sorption measurements on the solid in question. The Brunauer, Emmett and Teller (BET) equation is the most widely used equation to determine the surface area of coals. The BET equation uses the N₂ adsorption isotherm obtained at the temperature of liquid N₂ (77 K). However, there is
controversy concerning the validity of the BET equation. According to Mahajan (1984), the N₂ adsorption isotherm at 77 K does not give a reliable measure of the total surface area of materials containing an appreciable proportion of microporosity such as coals. This could be attributed to the fact that (1) N₂ molecules at 77 K do not possess enough kinetic energy to readily penetrate into coal micropores due to activated diffusion limitation and (2), the micropores undergo some decrease in their size at low temperatures.

To circumvent this problem, Seaton et. al. (1989) have recently proposed a new analysis method for the determination of the microstructure from N₂ adsorption measurements. This method, which is based on a molecular model for the adsorption of N₂ on porous carbon, allows the distribution of pore sizes to be determined over both the micropore and mesopore size ranges using a single analysis method. However, as in the case of BET theory, this molecular method is still based on the layer-by-layer filling of the pores by N₂.

Dubinin (1989) has proposed a concept based on the potential theory of Polayni which is now used for the determination of the microstructure of highly microporous materials. Unlike the BET theory, the Dubinin theory is based on the adsorption of the adsorbate in the micropores of carbon adsorbents consisting of the most probable slit-like, limited-size type due to the dispersion interactions between the adsorbate and adsorbent atoms as well as between the atoms of the adsorbed substances themselves. As a consequence of the presence of a force field due to above-mentioned dispersive and adsorption forces, the adsorbates, which are of similar size as the pore, adsorb in the micropores of activated carbon adsorbents resulting in the volume filling of the available micropore space, i.e., the field of adsorption forces. Because the chemical structure of activated carbon is composed mainly of benzene like rings, Dubinin (1975) recommended benzene as a reference adsorbate for characterizing activated carbon adsorbents.

Based on the theory of volume filling by the adsorbate in the case of microporous materials, use of adsorption isotherms of light normal alkanes for characterizing microporous activated carbons has been studied by Jaroniec et. al.
(1991). Analysis by means of the Dubinin-Radushkevich equation revealed the utility of the adsorption isotherms of ethane, propane and n-butane for describing the microporosity of activated carbons. The Author recommended that n-butane be used as a reference adsorbate for characterization of microporous activated carbons.

Following the pioneering work of Dubinin, various researchers examined the possibility of using different adsorbates for characterizing microporous materials. Adsorption of helium on activated carbon and activated charcoal has been measured in the pressure range 1-30 atm and in the temperature range 15-70 K by Duband et. al. (1987). A Clapeyron like law for the fictitious saturation vapor pressure above the critical temperature has been deduced experimentally from the measurements. This law has led to a fairly good generalized correlation for all experimental data in the framework of the Dubinin theory.

Garro et. al. (1987) studied the adsorption of N\textsubscript{2} (77 K) and CO\textsubscript{2} (273 and 298 K) on a series of activated carbons covering a wide range of burn-off, and observed that for carbons of low burn-off, the characteristic curve is unique and a common value of micropore volume can be deduced from N\textsubscript{2} (77 K) and CO\textsubscript{2} (273 K) adsorption. As burn-off increases, the micropore volume measured by CO\textsubscript{2} adsorption isotherm will be coincident with that measured by N\textsubscript{2} only if low-pressure data for N\textsubscript{2} are available. If this requirement does not hold, micropore volume values from N\textsubscript{2} adsorption will be larger than those from CO\textsubscript{2} adsorption. However, the micropore volume obtained from a N\textsubscript{2} adsorption isotherm will be similar to those from a hydrocarbon (such as benzene) adsorption. On the other hand, because of the higher temperature and much lower relative pressure range covered, micropore volumes as measured from CO\textsubscript{2} adsorption will be smaller since this measures the narrow microporosity.

2.8.2 Fourier transform infrared spectroscopy (FT-IR) in fuel science

FT-IR spectroscopy is one of the most versatile techniques available for providing analytical data on coal, coal chemistry and products of various coal utilization processes. Dispersive infrared spectroscopy (IR) has traditionally been an
important tool in coal characterization since most organic and mineral components absorb in the IR range. Discussions of applications to coal may be found in Lowry (1963), van Krevelen (1961), Friedel (1966) and references cited therein.

As a result of the advantages associated with the use of FT-IR which includes fast on-line data acquisition, baseline corrections, smoothing, spectral comparisons, spectral synthesis, factor analysis etc., investigators have started reexamine applications of FT-IR in fuel science and technology. Painter et. al. (1978a, 1978b) have proposed techniques for quantitatively analyzing mineral components in coals. Painter has also used FT-IR for studying coal oxidation (1980) and liquefaction products (1979a, 1979b). Solomon has considered FT-IR for determining organic constituents such as aliphatic and aromatic hydrogen (1981) and hydroxyl groups (1981). Applications of quantitative analysis of organic components have been applied to coal proximate analysis (1981), oil shale yields (1980), pyrolysis yields (1981) and coal structure (1981).

2.9 Kinetic modeling

Modeling of SO₂ adsorption on any adsorbent is usually performed to predict the relationship between the effluent concentration of the adsorbate and time-on-run (breakthrough curve). In the case of NOₓ removal kinetic modeling is performed in order to predict the breakthrough curve. A review of the kinetic modeling for the removal of both SO₂ and NOₓ using lignite, char and activated carbon is presented below.

2.9.1 Modeling of sulfur dioxide adsorption

To the best of our knowledge, no model is available in the open literature for the prediction of the breakthrough curve of SO₂ adsorption on lignite or lignite-derived char and activated carbon. However, models are available that describe the adsorption of gases on solids in packed beds.

These models depend on the rates of transfer of adsorbate to adsorbent, temperature of adsorption and equilibrium relationships between fluid phase...
concentration of the adsorbate and the corresponding solid phase concentration. In the case of the rate of transfer of adsorbate to adsorbent, the assumptions are that the rate of mass transfer from the fluid phase to the fixed solid particles depend on any combinations of (1) external film resistance, (2) pore diffusion, (3) surface diffusion and (4) adsorption of the adsorbate on the adsorbent.

In the case of temperature of adsorption, the process can be isothermal or non-isothermal. Mathematical treatment of the isothermal adsorption is available in the literature. The equilibrium relationships available in the literature represents both linear and non-linear situations.

Detailed mathematical treatment of the isothermal adsorption of dilute gases in packed columns was given by Thomas (1951) which considered pore diffusion as the controlling mechanism and was based on linear equilibrium relation. This model was expanded by Rosen (1952) to include the effect of external film resistance on the adsorption process. In the case of linear adsorption isotherm, analytical solution for the isothermal adsorption of a solute in a packed bed of porous solid was given by Rosen (1952) in his pioneering work.

Because a great majority of the equilibrium data is non-linear, Antonson (1967) modified Rosen's work to include a Langmuir type isotherm. Antonson, however, totally neglected the resistance of an external film surrounding the particle.

As the system of equations describing the adsorption system are most often highly non-linear, analytical solution becomes very complicated. So, solution of these systems have been calculated using numerical techniques. A numerical solution of the system of adsorption equations where pore diffusion is the controlling mechanism has been given by Garg and Ruthven (1974). They assumed Langmuir type adsorption isotherm to describe adsorption equilibrium. These authors also reported a numerical solution of the adsorption system where film resistance is the rate controlling mechanism (1975). The effect of the axial dispersion on the adsorption process was also incorporated in this model.
2.9.2 Modeling of NO\textsubscript{x} removal

NO\textsubscript{x} can be removed from flue gas by chemical reaction (with or without catalysts) or by adsorption using an adsorbent or by a combination of both. Kinetic models for the removal of NO\textsubscript{x} by chemical reaction alone are available in the literature (Miyamoto et. al., 1982; Anderson et. al., 1994). These models are based on either on Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach (Takagi et. al., 1977; Knoblauch et. al., 1985; Siddiqi and Tenini, 1981) or Eley-Rideal approach (Anderson et. al., 1994; Inomata et. al., 1978; Miyamoto et. al., 1979). Miyamoto et. al. (1982) studied the mechanism over V\textsubscript{2}O\textsubscript{5}, supported V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{4} catalysts by way of \textsuperscript{15}N tracer studies. On the basis of their experimental results they proposed a mechanism which is shown in Figure 2.3. More recently, a more detailed reaction scheme (shown in Figure 2.4) which includes the formation of N\textsubscript{2}O has been reported by Janssen et. al. (1987a; b). Many kinetic and mechanistic studies of the selective catalytic reduction of nitric oxide with ammonia in the presence of oxygen have been made.

No model is available in the literature regarding the adsorptive removal of NO\textsubscript{x} alone. However, as was mentioned previously in the case of SO\textsubscript{2} removal, a number of models are available that can describe the adsorption of a number of gases on various adsorbents in a packed column.

A good model for the adsorptive and reactive removal of NO\textsubscript{x} using activated carbon or impregnated activated carbon should be able to predict the shape of the breakthrough curve, breakthrough time and the yield. To the best of our knowledge, no such model is available in the literature. Only models that can predict the yield in such adsorptive and reactive removal of NO\textsubscript{x} based on LHHW approach have been reported in the literature (Richter, 1990; Junthgen, 1988).

In the case of the model reported by Richter, it has been shown that the most probable mechanism in the removal of NO by activated carbon in the presence of O\textsubscript{2} involves the oxidation of an adsorbed unstable (NO)\textsubscript{2}-complex by O\textsubscript{2}. Also, it has been shown that the surface reaction of NO with carbon surface oxide is the rate limiting step while NO-adsorption and NO\textsubscript{2}-desorption are in equilibrium. In addition,
Figure 2.3: The Mechanism of NO-NH₃ Reaction on Vanadium Oxide As Proposed by Miyamoto Et. Al. (1982)
Figure 2.4: Proposed Sequence of Reactions for the Reduction of NO by NH₃ Over a Supported Vanadia catalyst to Form N₂, H₂O and N₂O As Proposed by Janssen Et. Al. (1987a; b)
the inhibitory effect of water vapor has been incorporated in the mechanism.

On the other hand, the model by Juntgen et. al. (1988) concerns the reduction of NO by NH₃ in the presence of O₂ over activated carbon. Using the steady-state conversion data from an integral reactor, they derived a rate equation which includes the concentration of nitric oxide, oxygen and ammonia. This is given in equation.

All the rate equations that have been developed for nitric oxide removal processes use Langmuir-Hinshelwood classical kinetics. However according to Boudart (1956), the wide applicability of the Langmuir-Hinshelwood kinetics to real surfaces is questionable. In his opinion, the limitations of this technique are often more than compensated for by the added insight into reaction mechanism which can provide without undue complexity. The main drawback of using this technique for developing the rate equation lies in the lumping of various parameters into the final equation.

For traditional catalytic process technologies steady-state kinetic models are used, whereas for the models of processes with unsteady-state catalysts dynamic characteristics should be known. Kinetic aspects of heterogeneous catalysis have been considered previously in terms of the well-known Langmuir-Hinshelwood, Eley-Rideal, etc. mechanisms. Catalyst compositions and concentration of active centers were thought to be unchangeable and independent of reaction conditions. Boreskov's conception (1984) concerning the effect of reaction mixtures on catalyst properties has played an important role in the development of new kinetic concept for heterogeneously catalytic reactions.

Renken (1984) argued that the experimental observations can not be explained by averaging a spectrum of steady-state but are due to the surface dynamics. The dynamic behavior of individual steps of the overall reaction and of the reactor can be exploited to obtain performances and selectivities which can not be accomplished in steady-state operation and operating ranges of the reactor can be reached that are inaccessible under comparable steady-state conditions. However, to the best of our
knowledge no information concerning the unsteady-state rate equation for nitric oxide removal processes is available in the open literature.
3. EXPERIMENTAL

3.1 Scope

In this chapter, the design, construction and operation of the fixed bed reactors and apparatus, used to obtain data in this work, are described. Details of adsorbent preparation, characterization and evaluation of their adsorption performance are also described here.

3.2 Preparation of adsorbents

As-received lignite was processed to prepare four different adsorbents; namely, dried lignite, char, activated carbon and metal-impregnated activated carbons. Dried lignite was carbonized in order to prepare char which was subsequently activated to obtain activated carbons. A fixed bed micro-reactor was used for the preparation of these adsorbents. Metal-impregnated activated carbon adsorbents were prepared by impregnating activated carbon with various metal compounds. The preparation of lignite, char, activated carbon and metal-impregnated activated carbons will be discussed in this section.

3.2.1 Preparation of lignite

The lignite used in this study was obtained from the Saskatchewan Power Corporation (SPC), Regina, Canada. Dried lignite was prepared by drying the as received lignite from SPC in an oven at 90-100°C overnight and it was stored in a desiccator for subsequent use.

3.2.2 Preparation of chars

Dried lignite was carbonized to prepare char. The experimental rig used for carbonization and the operating conditions used will be discussed in this section.
3.2.2.1 Experimental rig for the preparation of the chars

Figure 3.1 shows the process flow diagram of the experimental rig used for the preparation of adsorbents. The carbonization experiments were performed in a stainless steel (SS-316), tubular reactor (25.4 mm ID and 450 mm overall length) placed coaxially in an electrically heated furnace. Lignite was supported on a stainless steel wire mesh screen located 300 mm below the reactor outlet. The temperature of the bed was controlled by placing two K-type thermocouples (T1 and T2), one at the inside wall of the reactor (T1, connected to the indicator) and the other at the center of the bed (T2, connected to the controller). The bed was 100 mm long and the temperature difference between the inside wall and the center did not vary by more than 2°C. The furnace temperature was controlled by a Series SR22 microprocessor-based auto-tuning PID temperature controller (supplied by Shimaden Co; Ltd, Tokyo, Japan) through the K-type thermocouple (T2) inserted into the center of the bed. This arrangement was capable of ensuring an accuracy of ±2°C for the furnace temperature.

Each batch of char was prepared by carbonizing 10 g of dry lignite in the size range of 4.5 to 5.6 mm (-3 1/2 + 4 sieve, Canadian standard) in flowing nitrogen (flow rate: 100 ml/min) at the desired carbonization temperature. The four temperatures used for carbonization were: 350, 410, 475 and 550°C, each at the carbonization holding times of 30, 75, and 120 min.

3.2.2.2 Typical carbonization run

A typical carbonization run was performed as follows: the reactor was packed with 10 g of dried lignite supported on a steel wire mesh. The reactor was heated at a constant heating rate of 8°C/min to the desired carbonization temperature in flowing (100 mL/min) nitrogen (99.995% purity, obtained from Linde) and was held at that temperature for the length of the desired carbonization holding time. The temperature at the center of the lignite-bed was recorded every 15 minutes during the carbonization experiments by a multichannel digital temperature indicator. At the end of this period, the reactor was cooled down to room temperature under flowing
Figure 3.1: Process Flow Diagram of the Experimental Rig
Used for Carbonization of Lignite and Activation of Char
nitrogen. The liquid and gaseous carbonization products passed through an ice-cold condenser to remove the liquid. The gaseous product was then collected over concentrated brine solution in a graduated cylinder. The volume of the gaseous product was recorded at the end of the carbonization experiment. Once the reactor cooled down to the room temperature, the char was taken out and weighed.

3.2.2.3 Analysis of the gaseous product evolved during carbonization

Gas samples (taken from the graduated cylinder with a gas tight syringe) were analyzed using a Carle GC series 500 chromatograph. Two different gas chromatographic analyses were made under the following conditions:

1. Analysis of hydrocarbon gases was performed with a 32 mm dia., 1.82 m long Chromosorb 102 60/80 column with temperature programming of 7°C/min from 40 to 200°C. A flame ionization detector (FID) was used with helium as the carrier gas.

2. Analysis of hydrogen was performed with a 32 mm dia., 2.74 m long molecular sieve 13X column and a thermal conductivity detector using a Carle GC series 500, which employed a hydrogen transfer system (HTS). Helium carrier gas was used as the carrier gas.

Knowing the density of the major gaseous components at standard conditions, their weight fractions for a particular experiment and the total volume of the carbonization gaseous product, the gas yields and compositions could be calculated and reported on a carrier gas (N₂) free basis. Detailed calculations and chromatograms for a typical case are shown in Appendix A.

3.2.3 Preparation of activated carbon

Chars, prepared by carbonization of lignite, did not show adequate gas adsorption capacity. In order to increase their adsorption capacity, chars were activated to prepare activated carbons. This section describes the experimental procedure and operating conditions used for activation of char.
3.2.3.1 Experimental rig used for activation

The experimental rig used in the preparation of activated carbon using CO₂ as the activation agent was similar to the one which was used for carbonization experiments.

In the case of CO₂ activation, CO₂ gas was dosed by a valve and measured by a flow meter. On the other hand, in the case of steam activation, nitrogen gas was passed through a bubbler containing water. The temperature of the water bath (bubbler) was 85 °C and was controlled by a microprocessor-based auto-tuning PID controller (Supplied by Shimaden Co Ltd., Tokyo, Japan) through a K-type thermocouple inserted into the heating block.

3.2.3.2 Typical activation run

Activated carbon was prepared by activating char at various activation temperatures (550, 650 and 750 °C) and activation times (15, 30, and 45 min). Both CO₂ and H₂O were used as activation agents under these sets of conditions.

Each activation experiment consisted of two steps. In the first step, lignite was carbonized to prepare char and the char was subsequently activated in the second step to prepare activated carbons. For this purpose, the char known to have the optimum physical or pore characteristics and highest SO₂ adsorption capacity was selected for activation. Optimum physical or pore characteristics of chars were estimated from micropore surface, volume, median pore diameter and percentage of micropores. Interestingly, the char which exhibited optimum physical characteristics also showed the highest SO₂ adsorption capacity. The preparation conditions for this char were: carbonization temperature, 475 °C; carbonization holding time, 120 min.

In order to prepare activated carbon, carbonization of lignite was carried out with a batch of 10 g of dried lignite at the optimum carbonization temperature (475 °C) and holding time (120 min) in flowing nitrogen (100 mL/min). At the end of the carbonization holding time, the flow of nitrogen was stopped and the bed was heated in flowing carbon dioxide or steam at a constant heating rate of 8 °C/min from the carbonization temperature (475 °C) to the desired activation temperature which
was either 550, 650 or 750°C. The reactor bed was held at the desired activation
temperature for the desired length of activation time (15, 30 or 45 min) with a flow
rate of CO₂ or N₂ saturated with water vapor of 150 mL/min. At the end of the
activation step, the reactor was cooled down to room temperature under flowing
nitrogen and the activated carbon sample was weighed. The total burn-off was
calculated by subtracting the weight of the activated carbon from the weight of dry
lignite used.

3.2.4 Preparation of metal-impregnated activated carbon

It has been reported that entirely different kinds of catalysts such as
CuO/Al₂O₃ can also be used for removal of SO₂ and NO from the flue gases (Richter,
1990). There are also indications that impregnation with metals improve the
adsorption capacities of activated carbons (Grzybek, 1992). In the case of any
impregnated catalyst, dispersion of the active material is very important for the
optimum operation of the catalyst. Dispersion of active material in a microporous
catalyst support depends on pore size distribution. Results obtained from the physical
characterization of lignite, chars and activated carbons showed that activated carbons
contained the highest microporosity with a larger average pore size as compared to
that of lignite and chars. Consequently, activated carbon was selected as the support
for the preparation of metal-impregnated activated carbon catalysts. In order to
obtain uniform distribution as well as to avoid surface coating of the active material
low metal loading (1 wt% metal) was used for preparing metal-impregnated activated
carbon catalysts.

3.2.4.1 Materials

Four catalysts, namely iron, copper, cobalt and nickel-impregnated activated
carbon catalysts were prepared by impregnating activated carbon with aqueous
solutions of the respective metal nitrate solutions. The prepared catalysts were
analyzed at the Catalysis and Chemical Reaction Engineering Laboratory in the
Department of Chemical Engineering of University of Saskatchewan, Saskatoon, to determine their physical characteristics.

The sources of copper, iron, cobalt and nickel, respectively, were copper nitrate trihydrate [Cu(NO$_3$)$_2$$\cdot$3H$_2$O; ACS grade, obtained from Fisher Scientific Co], ferric nitrate nonahydrate [Fe(NO$_3$)$_3$$\cdot$9H$_2$O; AnalR grade, obtained from BDH chemicals], cobaltous nitrate hexahydrate [Co(NO$_3$)$_2$$\cdot$6H$_2$O; AnalR grade, obtained from BDH chemicals] and nickel nitrate hexahydrate [Ni(NO$_3$)$_2$$\cdot$6H$_2$O; AnalR grade, obtained from BDH chemicals].

3.2.4.2 Impregnation procedure

Impregnated adsorbents/catalysts, containing 1 wt% of metal, were prepared in the following way: the activated carbon support was dried at 100-110°C overnight and then impregnated with an aqueous solution of metal nitrate of known concentration for 24 hours. The resulting catalysts were dried at 110-120°C overnight.

3.3 Characterization of adsorbents

Evaluation of the microporosity and surface functional groups at each stage of preparation of char and activated carbon from lignite was important in order to optimize the development of the adsorbent. This was done by physical and chemical characterization of lignite, char and activated carbon adsorbents. While microporosity of the adsorbent was determined by physical characterization of the adsorbent, surface functional groups were determined by chemical analysis. Physical characterization involved the estimation of micropore surface area, pore volume, pore size and pore size distribution. The chemical methods involved estimation of carbon, hydrogen, nitrogen and oxygen by CHN elemental analysis and identification of functional groups by FT-IR spectroscopy. In addition, in the case of metal-impregnated activated carbon adsorbents, the oxidation state of the active metal species was determined by temperature programmed reduction (TPR) technique. These will be described in this section.
3.3.1 Physical characterization of lignite

Micropore surface area, pore volume, pore size, and pore size distribution of lignite were measured using an accelerated surface area and porosimetry equipment (ASAP 2000, supplied by Micromeritics). Two types of adsorbates, namely, N\textsubscript{2} and CO\textsubscript{2}, were used at analysis temperatures of 77 K and 273 K, respectively. Prior to analysis, each sample was degassed at an appropriate temperature to a vacuum of 0.003 mm - 0.005 mm Hg for 24 hours. The degassing temperatures tested were 75, 125 and 175°C.

In this work, the Dubinin-Astakhov equation (Dubinin, 1989) was used for the calculation of the micropore surface area and limiting micropore volume. Micropore volume, median pore diameter and differential pore volume were estimated by the Horvath-Kawazoe method (Horvath and Kawazoe, 1983).

3.3.2 Physical characterization of char and activated carbon

Similar physical characterization procedures were employed to determine microporosity in chars and activated carbons. However, in this case, the char and activated carbon samples were degassed at 125°C for 24 hours and physical characterization was carried out using only the CO\textsubscript{2} adsorption isotherm obtained at 0°C (273 K). These were the best analysis conditions established from the physical characterization of lignite.

3.3.3 Physical characterization of metal-impregnated activated carbons

A similar characterization procedure was also followed to characterize metal impregnated activated carbon adsorbents which were prepared by impregnating an activated carbon support with metal nitrate solutions. Before use in actual adsorption experiments, these catalysts were calcined in order to convert the metal nitrates into their respective oxides. This (calcination) usually results in the redistribution of the active materials into the support material. Therefore, it was decided to physically characterize both calcined and uncalcined metal-impregnated catalysts. This was
necessary in order to examine the changes in the porosity of the adsorbents due to calcination.

3.3.4 Carbon-hydrogen-nitrogen elemental analysis

Since coal is a heterogeneous mixture of many organic and inorganic materials, it is important to have analytical methods to measure the organic constituents accurately and thus to be able to follow their path through various stages of lignite utilization. For example, knowledge about the C/H, O/H atomic ratios could help in understanding the relative structural changes of the lignite due to carbonization and activation. In order to determine carbon, hydrogen, nitrogen and oxygen content of lignite, char and activated carbons, elemental analysis was carried out. Carbon, hydrogen and nitrogen were determined in a Perkin Elmer 2400 CHN elemental analyzer. Oxygen was estimated by difference. Ash content was not determined.

3.3.5 Temperature programmed reduction studies of metal-impregnated activated carbons

In the case of impregnated catalysts, it is known that the oxidation state of the active material play an important role in catalyzing the desired reaction (Acres et. al., 1981). Therefore, determination of the oxidation state of the active material is important. This is usually carried out using the temperature programmed reduction (TPR) technique. In this process, the reduction of a reducible material with hydrogen, which is a topochemical reaction, supplies information about the change in the state of the material with temperature. Consequently, the temperature programmed reduction technique was employed for the verification of the nature of the species present in the catalysts.

The analyses were performed at atmospheric pressure in a conventional flow system which is shown in Figure 3.2. The equipment and procedure used were similar to ones described by Varma et. al. (1984). The experiments consisted of placing 1g
Figure 3.2: Conventional TPR/TPD System
[1, thermal conductivity cell; 2.1, reduction valves; 2.2, deoxygenation catalyst; 2.3, dehydration catalyst; 2.4, cold trap; 2.5, gas flow switch; 2.6, vent; 3, quartz reactor; 4, furnace; 5, temperature programmer; 6, recorder; 7, thermocouple]
of the sample in the reactor and heating it in the reducing gas (5% \( \text{H}_2 \), balance \( \text{N}_2 \)) stream at a linearly programmed rate of 4° C/min from 25 to 700°C.

Isothermal reduction of the metal-impregnated adsorbents consisted of placing 1 g of the calcined sample in the reactor, reducing it in-situ at the required temperature in pure hydrogen at a flow rate of 60-75 mL/min for 2h, and allowing it to cool down to the temperature required for adsorption experiment.

### 3.3.6 FT-IR spectroscopic analysis

Carbonization and activation of coal result in the changes in the structure of the parent coal material (Hassler, 1974). While carbonization results in polycyclization in the parent material, subsequent activation results in the formation of various functionalities such as hydroxyls, ketones etc. on the surface of the activated carbon. These functional groups have been found to participate (Davini, 1990) in the adsorption of \( \text{SO}_2 \) by activated carbons. Therefore, it was important to conduct experiments which can provide information concerning the carbon surface groups. It is now known that Fourier transform infrared spectroscopy (FT-IR) is one of the most versatile analytical techniques available for the study of fossil fuel structure due to its high sensitivity, and dispersive FT-IR has traditionally has been employed as an important tool in the characterization of carbonaceous fuels since most organic and mineral components, which are present in lignite, and other lignite-derived adsorbents, absorb in the IR.

Infra red spectra of lignite, chars and activated carbons were observed in the following manner. FT-IR transmission spectra of lignite, chars and activated carbons were obtained for finely ground samples pressed in KBr pellets. A small sample (typically 0.50 mg) of this finely ground sample was weighed (± 0.01 mg) in a dry box and added to a weighed amount (about 300 mg determined to ± 0.1 mg) of KBr. The KBr and lignite (or other adsorbents) were then mixed by grinding for 30 seconds and pressed into a pellet in an evacuated die under 20,000 lbs pressure.

In the literature (Painter and Coleman, 1980), the diffuse reflectance technique has been reported which was used to obtain the spectrum in the situations where KBr
would restrict the access to the coal or coal-derived materials. The diffuse reflectance spectrum of the diluted samples were recorded on an FT-IR spectrometer operated with a resolution of 4 cm\(^{-1}\) and an accumulation of 256 scans, using finely powdered KBr as a reference. Finally, the observed diffuse reflectance was converted into the Kubelka-Munk function which was subsequently plotted against wavenumbers.

3.4 Adsorbent performance evaluation

In order to evaluate SO\(_2\) and NO adsorption capacities, adsorbents were subjected to adsorption experiments in a fixed-bed adsorber.

3.4.1 Experimental rig for the evaluation of the adsorbent performance

Figure 3.3 shows the process flow diagram of the experimental rig used for adsorption studies. The adsorption experiments were performed in a stainless steel (SS-316) tubular column (12.7 mm ID and 400 mm overall length) placed in an electrically heated furnace. The furnace temperature was controlled by a series SR22 microprocessor-based auto-tuning PID temperature controller (supplied by Shimaden Co Ltd., Tokyo, Japan) through a K-type thermocouple inserted into a heating block placed concentrically within the furnace. Separate thermocouples were used to monitor the temperatures of the inside and outside walls as well as the inlet of the reactor. This arrangement was capable of ensuring an accuracy of \(\pm 2^\circ\)C for the adsorbent bed temperature.

The flow rates of various gases used for the adsorption experiments (such as SO\(_2\), NO, O\(_2\) and N\(_2\)) were adjusted using needle valves and the flows were measured by flow meters. While SO\(_2\) flow was measured by a Flow Trak digital mass flow meter, the flow of N\(_2\) gas was monitored by a type 8141 Matheson transducer connected to a mass flow meter readout model 8143. The flow of NO and O\(_2\) flow were measured by rotameters.
Figure 3.3: Process Flow Diagram of the Experimental Rig

Used for Adsorption Experiments
3.4.2 Operating variables for adsorption experiments

In the sulfur dioxide adsorption experiments with lignite, the operating ranges of the various variables or parameters are given below:

- Adsorption temperature: 75, 125 and 175°C
- Bed length: 5.5 cm
- Gas flow rate: 40, 70 and 100 mL/min
- Flow distributor length: 4 cms
- Flow distributor diameter: 5.6 mm (glass)
- Adsorbent particle size: 2.0, 3.4 and 5.6 mm
- Packing particle diameter: 2.0, 3.4 and 5.6 mm (glass)
- Influent gas composition:
  - SO$_2$: 1000, 3000 and 5000 ppm
  - N$_2$: Residual

In order to achieve optimum operation of the adsorption process, results of the sulfur dioxide adsorption experiments with lignite were used to select the operating conditions for subsequent sulfur dioxide adsorption experiments with char and activated carbon. For example, it was observed that at low influent sulfur dioxide concentration (1000 ppm) and long residence time (10 sec), broadening of the SO$_2$ breakthrough profile on lignite was observed which significantly reduced the adsorption capacity of lignite. Therefore, in subsequent adsorption experiments involving other adsorbents such as lignite derived chars, activated carbons and metal-impregnated activated carbons, the operating conditions were specified as follows: adsorption temperature, 125°C; particle size, 4 mm; influent SO$_2$ concentration, 5000 ppm; and residence time, 4 sec. However, different influent gas compositions were used in other phases of this project. These are given below:

1. SO$_2$ adsorption in the presence of O$_2$ (Phase 4): SO$_2$, 3000 ppm; O$_2$, 6.5 vol% and N$_2$, balance.
2. NO adsorption experiments in the absence of oxygen (Phase 5): NO, 1100 ppm; N$_2$, balance.
3. NO adsorption experiments in the presence of oxygen (Phase 5): NO, 400 ppm; O$_2$, 6.5 vol% and N$_2$, balance.
4. NO adsorption experiments in the presence of sulfur dioxide and oxygen (Phase 6) NO, 400 ppm; SO$_2$, 3000 ppm; O$_2$, 5 vol% and balance N$_2$.

3.4.3 Procedure for evaluation of adsorbent performance

A typical adsorption run was performed as follows: the reactor was packed with 1 g of pre-dried adsorbent such as lignite, char, activated carbon or metal-impregnated activated carbon supported on a stainless steel wire mesh. Adsorbent particles were mixed with inert materials (glass particles) of similar size to increase the bed height and to disperse heat uniformly. Flow distributors, which were inert materials (glass particles), were used at the inlet to obtain uniform flow of gas mixture. The size of the flow distributors were large compared to the inert packing material as well as adsorbents (5.6 mm). The reactor was heated to the desired adsorption temperature in flowing N$_2$ gas (99.995% purity, obtained from Linde) and was held at that steady-state temperature for one hour. Then, the nitrogen gas flow was stopped and the influent gas mixture was passed through the adsorbent bed at the desired flow rate. The temperatures at the center of the adsorbent bed, reactor inlet and the inside wall of the reactor were recorded every 5 minutes during the adsorption experiments using a multichannel digital temperature indicator. The effluent stream was analyzed at 5 min intervals to determine the effluent gas composition. This analysis was carried out in an on-line Hewlett-Packard 5890A gas chromatograph using a Chromosorb-102 60/80 column with a thermal conductivity detector (TCD) with helium as the carrier gas. Details of the gas chromatographic analysis of the adsorber effluent is given below.

3.4.4 Analysis of adsorbent effluent stream

In order to evaluate the adsorption performance of adsorbents, it is important to analyze effluent gas composition quantitatively at regular intervals. This was done by using an on-line gas chromatograph which took samples from the column through the manipulation of two 10 port valves.
Usually, quantitative analysis of any gas chromatographic (GC) peak is carried out by calibrating the GC with a standard mixture containing known amounts of the components. It is known that polar components such as SO₂ and NO are very reactive with most chromatographic column materials. Consequently, the calibration standard of GC keeps on changing with time due to deactivation of the column. In this work, to avoid this basic problem, instead of a pre-calibration, the GC was calibrated at the beginning of each adsorption experiment. This was done by analyzing the influent gas mixture by by-passing the reactor with the help of two needle valves which are shown in Figure 3.3 (X-141, X-142). Subsequently, as mentioned earlier, the effluent stream was analyzed at 5 min intervals to determine the effluent gas composition against the influent concentration.

In the literature, various chromatographic columns have been reported for analyzing mixtures of SO₂, NO, O₂ and N₂. However, during the selection of any gas chromatographic column, the analysis time (time necessary to complete one chromatographic run), the resolution of the desired peak and the sensitivity of the analysis should be considered. In the present study, while analysis of SO₂ did not pose any major analytical problem, NO analysis posed several problems which made the quantitative analysis of NO difficult.

In the case of sulfur dioxide (SO₂) adsorption experiments in the presence and absence of O₂, the analysis of SO₂ from a mixture of SO₂, N₂ and/or O₂ in the effluent stream was carried out every 5 min by a 32 mm dia., 1.82 m long Chromosorb-102 60/80 column. A TCD detector was used at high sensitivity setting with helium as the carrier gas. Gas chromatographic analysis temperature was 90°C.

A basic problem associated with the analysis of NO by gas chromatography was the severe tailing of the NO peak which reduced the sensitivity of the instrument. Various other columns were tested for the analysis of NO which included Molecular Sieve, Porapak Q, Porapak Q and R in series and Chromosorb 102. Molecular Sieve column showed tailing of NO peak. Use of combination of Porapak Q and Porapak R in series eliminated tailing of the NO peak. However, the analysis time was long. This was not acceptable because after NO comes out of the adsorbent bed, its
concentration in the effluent stream goes up very rapidly. Consequently, if analysis of the effluent stream by GC column takes a long time, the changes in the NO concentration between two chromatographic experiment could not be measured. In the case of Chromosorb 102 column though there was no tailing of NO but the separation between the NO and N₂ peaks was very poor. However, good separation between NO and N₂ was achieved when longer Chromosorb 102 column was used. For NO adsorption experiments in the presence and absence of O₂, nitric oxide was analyzed by a 32 mm dia., 6.1 m long Chromosorb-102 60/80 column with the help of a TCD detector. The analysis temperature used was 30°C. In the case of gas mixtures containing both sulfur dioxide and nitric oxide, the analysis temperature was 0.35°C. The details concerning the operating conditions for the gas chromatograph are given in Appendix B.

3.4.5 Construction of breakthrough curves

SO₂ and NO adsorption capacities of lignite and lignite-derived adsorbents were evaluated by generating experimental breakthrough curves. Breakthrough curves showed the history of the effluent concentration of the adsorbate (such as SO₂ in the case of sulfur dioxide adsorption experiments) with respect to time. In order to generate experimental breakthrough curves, effluent concentrations, which were measured by GC analyses, were plotted against time. These breakthrough curves were analyzed to find the breakthrough time which corresponded to the time on run when the effluent concentration reached the desired level (50 ppm for NO and 100 ppm for SO₂).

3.5 Experiments to examine the potential of nascent hydrogen for NOₓ reduction

In the Catalysis and Chemical Reaction Engineering Laboratory of the University of Saskatchewan, a very efficient catalyst was developed recently which is very active for methanol decomposition and reforming and is very selective towards the production of very high purity hydrogen.
In the literature it has been reported that NO\textsubscript{x} can not be reduced by methanol. It was therefore decided to study the potential of the methanol decomposition or reforming catalyst for NO\textsubscript{x} reduction using the hydrogen stored in methanol.

### 3.5.1 Experimental rig for the evaluation of the adsorbent performance

Figure 3.4 shows the process flow diagram of the experimental rig used for reduction of NO\textsubscript{x} using methanol. The set up consisted of a fixed bed reactor, a device for the preparation of the gas mixture, and temperature control and analysis of NO, O\textsubscript{2}, H\textsubscript{2}, N\textsubscript{2} and hydrocarbon gas concentrations.

The reduction experiments were performed in a stainless steel (SS-316) tubular reactor (12.7 mm ID and 350 mm overall length) placed in an electrically heated furnace. The furnace temperature was controlled by a series SR22 microprocessor-based auto-tuning PID temperature controller (supplied by Shimaden Co Ltd., Tokyo, Japan) through a K-type thermocouple inserted into a heating block placed concentrically within the furnace. A separate thermocouple was used to monitor the temperature of the outside wall of the reactor. This arrangement was capable of ensuring an accuracy of ±2°C for the adsorbent bed temperature.

The gases NO, O\textsubscript{2} and N\textsubscript{2} were dosed by valves and measured by flow meters. NO and O\textsubscript{2} flow were measured by rotameters. Methanol and water mixture was pumped from a reservoir into a vaporizer using a syringe pump (NYC-13 D3 supplied by Bodine Electric Company, Chicago) where it was vaporized and subsequently mixed with an NO\textsubscript{x} and O\textsubscript{2} gas mixture in a mixing vessel. The temperature of the vaporizer was controlled by a microprocessor-based auto-tuning PID controller (Supplied by Shimaden Co Ltd., Tokyo, Japan) through a K-type thermocouple inserted into the heating block.

### 3.5.2 Operating variables for NO\textsubscript{x} reduction experiments

NO\textsubscript{x} reduction was performed simultaneously with the production of hydrogen from methanol in the presence and absence of oxygen over the Mn-promoted Cu-Al coprecipitated catalyst at atmospheric pressure with reaction temperatures of 200,
Figure 3.4: Schematic Diagram of Experimental Rig for the reduction of Nitric Oxide

[1- N₂ or NO/N₂, 2- 5 % H₂ in N₂, 3- pressure gauge, 4- on/off valves, 5- bubbler, 6- air, 7- deoxygenation/dehydration catalyst, 8- needle valve, 9- vaporizer, 10- temperature indicator, 11- temperature controller, 12- fixed bed reactor, 13- catalyst bed, 14- heating block, 15- electrically heated furnace, 16- insulator, 17- water cooled condenser, 18- gas/liquid separator, 19- gaseous products, 20- liquid products, 21- gas chromatograph, 22- fume hood].
250 and 300°C, respectively. Each run was performed with 1 g of catalyst of 2 mm average particle size mixed with 4 g of pyrex glass of the same average particle size. The catalyst was activated in-situ by reduction using 5% H₂ in N₂ at 300°C for 2 h prior to a test run. In the absence of oxygen, the influent NOₓ concentration and NOₓ/N₂ flow rate were 950 ppm and 200 mL/min, respectively. An NOₓ influent concentration of 875 ppm, and NOₓ/N₂ flow rate of 200 mL/min, an O₂ influent concentration of 5 mol% and an air flow rate of 30 mL/min were used for the experiments in the presence of oxygen. In each case, the reductants tested were methanol-water mixtures with molar ratios of 1:0, 1:1 an 1:3 at a flow rate of 0.05 mL/min.

3.5.3 Procedure for evaluation of catalyst performance for the NOₓ reduction

A typical reduction experiment was performed as follows: the catalyst mixed with pyrex glass beads was loaded into the reactor and reduced in-situ. Hydrogen production from the methanol reaction was started by pumping the reductant of desired methanol-water molar ratio through the vaporizer (maintained at about 250°C) and then through the reactor. When the reactor stabilized at the desired reaction temperature, NOₓ alone (for the experiments in the absence of oxygen) or NOₓ and air (for the experiments in the absence of oxygen) were introduced into the reactor at the specified flow rates.

The reaction products were analyzed on-line using a gas-chromatograph (Model HP 5890) with a Porapak Q column in series with a Porapak R column, a thermal conductivity detector (TCD) equipped with a high/low sensitivity switch, and with nitrogen as the carrier gas. Because of its low concentration, NOₓ was analyzed with the TCD switched to the high sensitivity mode whereas other components were analyzed with the TCD in the low sensitivity mode. Analysis temperature of 200°C was used. The detection limit of NOₓ was 0.005%.
4. Results and Discussion

Section 4.1 includes the results obtained from preliminary work which involved establishment of the analysis scheme for gas chromatographic determination of sulfur dioxide (SO$_2$) and nitric oxide (NO) concentrations and establishment of the physical characterization technique for determination of the microporosity of various adsorbents.

Section 4.2 presents the results of carbonization and activation experiments performed to prepare char and activated carbon from lignite. This section deals with the development of microporosity during carbonization of lignite and activation of char and discusses the implications of this on the SO$_2$ adsorption characteristics. The preparation and physical characterization of metal-impregnated activated carbons are discussed in Section 4.3.

Performance studies of various metal-impregnated activated carbon adsorbents for the removal of SO$_2$ (Section 4.4) and NO (Section 4.5) has resulted in the development of catalysts which are more efficient as compared to those reported in the literature. In general, presence of O$_2$ and SO$_2$ has been reported to affect NO removal performance of many catalytic systems adversely (Bosch and Janssen, 1987). High NO removal performance of the metal-impregnated activated carbons, even in the presence of O$_2$ and SO$_2$, signified a necessary change for further study of the removal of NO by catalytic oxidation of NO to NO$_2$, or by reactive adsorption, as an alternative to conventional SCR technology for the removal of NO from smaller facilities where concentration of nitric oxide is not very high.

The kinetic modeling of SO$_2$ adsorption and NO reaction has provided a better understanding of the rates of SO$_2$ adsorption and NO reaction (Section 4.7) on lignite, char and activated carbon.
The use of methanol for the catalytic reduction of NO at low temperatures was very successful and signified a necessity for further study of the selective catalytic reduction of NO using methanol or other oxygenated hydrocarbons in order to develop a better SCR system to meet the challenge of increasing NO emission restrictions.

4.1 Phase 1: Preliminary work

The objective of this phase was to establish various analytical procedures which involved the establishment of a physical characterization scheme for evaluating microporosity of the adsorbents at various stages of their preparation and a gas chromatographic analysis scheme to determine the concentration of sulfur dioxide and nitric oxide in the adsorber effluent stream.

4.1.1 Physical characterization of coal

Pores in coal are distinguished according to the IUPAC nomenclature. The IUPAC nomenclature that will be used here as well as in subsequent discussions is as follows: (i) macropores: pores which have diameter \( >500 \text{ Å} \) or 50 nm, (ii) mesopores: pores which have diameters in the range of 20-500Å or 2-50 nm, (iii) supermicropores: pores which have diameters in the range of 10-20Å or 1-2 nm and, finally, (iv) ultramicropores: pores having diameters in the range of \( <10\text{ Å} \) or \(<1\text{ nm} \) (Mahajan, 1984).

Coals have an aperture-cavity type of porosity. Entrance to the pore system is determined by the aperture size and the extent of adsorption is determined by the cavity size. It has been pointed out by Mahajan (1984) that details of the pore structure influence the behavior of a coal more directly than does virtually any other property. Therefore, for the quantitative physical characterization of coal pore structure, one needs to estimate micropore surface area, pore volume, pore size and pore size distribution. Conventionally, displacement of gases and liquids by coals is used to measure their densities and pore volumes, whereas physical adsorption of
gases is used to measure their surface areas, pore volumes, pore sizes and pore size distributions.

4.1.1.1 Effect of adsorbate

As mentioned earlier, physical adsorption of gases is used to measure physical characteristics of coal and other coal-derived microporous materials. Prior to physical adsorption experiments, coal samples are degassed at a particular temperature (degassing temperature) for a certain length of time (degassing time) to drive off trapped gases using high vacuum. The degassed samples are then subjected to adsorption experiments at a specific temperature (analysis temperature) using a reference adsorbate. The physical characteristics thus measured have been found to depend on various parameters, namely: heat-treatment conditions used to dry coals prior to their physical characterization; degassing temperature and time used before the coal sample is subjected to the actual gas adsorption experiments; and adsorption temperature, gas (adsorbate) and equilibrium time allowed during the adsorption experiments. The objective of this study was to establish a reliable methodology for physical characterization of various adsorbents.

Our work involved detailed physical characterization of lignite using both nitrogen and carbon dioxide as the adsorbates. The physical characteristics of lignite measured by both adsorbates are shown in Table 4.1. It can be seen from Table 4.1 that the surface area of lignite as measured by the nitrogen adsorption experiment at 77 K (-196°C) was 2.7 m²/g for a degassing temperature of 75°C. On the other hand, for the same degassing temperature, surface areas of lignite measured from carbon dioxide adsorption isotherms were 25.5 and 20.0 m²/g for analysis temperatures of 273 and 303 K, respectively. Micropore volumes of lignite, estimated from nitrogen adsorption isotherms also were found to be very small (0.002 cc/g) as compared to those obtained from carbon dioxide adsorption experiments (0.013 and 0.009 cc/g for the adsorption temperatures of 273 and 303 K, respectively). It was thus assumed that at an analysis temperature of 77 K, nitrogen molecules were unable to enter into
Table 4.1  Physical Characteristics of Lignite Determined From CO₂ and N₂ Adsorption Isotherms

<table>
<thead>
<tr>
<th>Degas temp., °C</th>
<th>Adsorption temp., °C</th>
<th>Adsorbate gas</th>
<th>Method of analysis</th>
<th>Micropore surface area, m²/g</th>
<th>Micropore volume, cc/g</th>
<th>Horvath-Kawazoe:</th>
<th>Median pore diameter, Å</th>
<th>Pore size distribution, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>75°C</td>
<td>0°C</td>
<td>CO₂</td>
<td><strong>Dubinin-Astakhov:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25.5</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.5</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26.6</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.0</td>
<td>0.009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>14.9</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.8</td>
<td>0.010</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.7</td>
<td>0.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>125°C</td>
<td>0°C</td>
<td>CO₂</td>
<td><strong>Dubinin-Astakhov:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175°C</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0</td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.18</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07</td>
<td>0.011</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.010</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
<td>0.0005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>175°C</td>
<td>0°C</td>
<td>CO₂</td>
<td><strong>Dubinin-Astakhov:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175°C</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.3</td>
<td>9.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.8</td>
<td>11.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.0</td>
<td>8.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.9</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.4</td>
<td>6.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.2</td>
<td>12.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>-196°C</td>
<td>N₂</td>
<td><strong>Horvath-Kawazoe:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.4</td>
<td>10.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.8</td>
<td>9.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.5</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>125°C</td>
<td>CO₂</td>
<td><strong>Horvath-Kawazoe:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125°C</td>
<td>36.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36.1</td>
<td>36.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36.1</td>
<td>36.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>54.1</td>
<td>54.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.0</td>
<td>50.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>67.7</td>
<td>67.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.0</td>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>175°C</td>
<td>CO₂</td>
<td><strong>Horvath-Kawazoe:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>175°C</td>
<td>16.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.3</td>
<td>16.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.5</td>
<td>13.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.4</td>
<td>18.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.1</td>
<td>18.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>16.7</td>
<td>16.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60.0</td>
<td>60.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>25°C</td>
<td>CO₂</td>
<td><strong>Horvath-Kawazoe:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25°C</td>
<td>4.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.2</td>
<td>5.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1</td>
<td>4.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.2</td>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.1</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20.0</td>
<td>20.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75°C</td>
<td>25°C</td>
<td>CO₂</td>
<td><strong>Horvath-Kawazoe:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25°C</td>
<td>29.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>24.9</td>
<td>24.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35.5</td>
<td>35.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.4</td>
<td>13.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.6</td>
<td>12.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
all the pores of lignite. This assumption was further substantiated from the results concerning median pore diameter. From Table 4.1 it can be seen that the median pore diameter of lignite was estimated to be 12.2 Å using nitrogen adsorption isotherms whereas carbon dioxide adsorption isotherms estimated significantly smaller median pore diameters (9.3 and 7.9Å at analysis temperatures of 0 and 30°C, respectively, at a degassing temperature of 125°C). Table 4.1 also shows micropore size distribution of lignite measured using nitrogen as well as carbon dioxide adsorption isotherms. It can be seen from the pore size distribution that nitrogen molecules were unable to penetrate the micropores of lignite, especially the pores below 10Å. Therefore, micropore surface area and volume measurement using nitrogen adsorption isotherms did not give a true estimate of the total surface area of lignite and thus nitrogen as an adsorbate did not produce reliable results for the physical characterization of lignite and other microporous adsorbents. Consequently, carbon dioxide was selected as the adsorbate for subsequent physical characterization experiments.

4.1.1.2. Effect of degassing temperature

Prior to measuring the physical characteristics of lignite by gas adsorption, it is essential to remove trapped gas and water present in lignite without changing its structure. For this purpose, coals are usually dried and degassed at 105 to 110°C. In the literature it has been reported (Mahajan, 1984) that this drying procedure poses problems for lower rank coals such as lignite. For example, in such coals, thermal decomposition of functional groups to yield water and carbon dioxide can commence at temperatures below 100°C. The author also reported that drying and degassing of lignites at temperatures as low as 110°C can change their structure, and adversely affect their surface area and adsorption characteristics. Even in spite of these limitations, degassing at 110°C is still the most practical approach to dry coal samples. In our work, sulfur dioxide adsorption characteristics of lignite were planned to be evaluated in the temperature range of 75 to 175°C and also were intended to be correlated with the physical characteristics of the adsorbents. Therefore, it was
necessary to have a knowledge of the physical characteristics of lignite at those temperatures in order to develop a better understanding of the structure of lignite at the temperatures where they would be used for sulfur dioxide adsorption experiments. Therefore, three degassing temperatures were chosen and those were: 75, 125 and 175° C.

Table 4.1 gives the physical characteristics of lignite, obtained from carbon dioxide adsorption isotherms, for every possible combination of two different adsorption temperatures (0 and 30°C) and three different degassing temperatures (75, 125 and 175°C). It can be seen from the Table that an increase in degassing temperature from 75 to 175°C did not result in any significant changes in the measured micropore surface areas and micropore volumes of lignite. However, at an adsorption temperature of 0°C the median pore diameter increased monotonically over the degassing temperature range used. It also can be seen from the pore size distribution that, even though the increase in the degassing temperature from 75 to 125°C did not result in any significant change in the pore size distribution, a further increase in the degassing temperature to 175°C resulted in an increase in the fraction of mesopores. This was attributed to the enlarging of existing supermicropores into mesopores due to degassing of lignite at 175°C. Consequently, a degassing temperature of 75-125°C was selected. An adsorption temperature of 125°C was used in most of the SO₂ and NO adsorption experiments, and a degassing temperature of 125°C was selected for subsequent physical characterization experiments.

From this work, the following experimental conditions were selected for subsequent physical characterization:

| Adsorbate for gas adsorption analysis | CO₂ |
| Degassing temperature               | 125°C |
| Degassing time                      | 24 h. |
| Analysis temperature                | 273 K |
4.1.2 Gas chromatographic analysis

The adsorption capacities were evaluated by generating breakthrough curves which showed changes in the effluent sulfur dioxide and nitric oxide concentration with time. This was done by on-line chromatographic analysis of the effluent stream at regular time intervals. It was therefore necessary to separate sulfur dioxide (1000-5000 ppm), nitric oxide (400-1100 ppm), and oxygen from nitrogen in a chromatographic column. It was also necessary to collect as many data points of the effluent sulfur dioxide and/or nitric oxide concentration as possible. Therefore, another important parameter considered was the chromatographic run time necessary for analysis of those gases. While analysis of sulfur dioxide from a mixture of sulfur dioxide, oxygen and nitrogen did not pose any major problem, the nitric oxide analysis from a mixture of nitric oxide, nitrogen and oxygen, posed several problems.

A basic problem associated with the analysis of nitric oxide by gas chromatography was the tailing of the nitric oxide peak which reduced the sensitivity of the instrument and made quantitative analysis difficult. In the literature, various columns such as Molecular sieve 5A and Porapak-Q have been reported for separating nitric oxide from nitrogen without tailing in a reasonable chromatographic run time. However, nitric oxide concentrations used in those experiments were as high as 5%. In this work, both the above columns were tried. In the case of the Porapak-Q column (8 ft), the reproducibility of the column for the quantitative estimation of nitric oxide was poor. Improved results were obtained by the use of a longer Porapak-Q column, but again the resolution among nitric oxide, nitrogen and oxygen was not satisfactory. On the other hand, Molecular Sieve 5A column showed tailing and poor separation between nitrogen and nitric oxide peaks. In addition, the chromatographic run time necessary to carry out the desired analysis reached an unacceptable level. Consequently, those columns (Porapak-Q and Molecular Sieve 5A) were found unsuitable for the quantitative estimation of trace amount of nitric oxide in the adsorber effluent stream.
In the present work, chromatographic experiments were carried out using Chromosorb-102 column in order to determine the concentration of nitric oxide with good separation between nitrogen and nitric oxide. The column was 24-ft. (7.31m) long stainless steel tubing with an I.D. of 0.1 in. It was washed with reagent grade acetone and dried with air before packing to remove residual oil and grease. After packing with 60-80 mesh Chromosorb-102, the two ends were plugged with a short length of glass wool.

Before using the column for analysis, it has to be activated by passing a mixture of 1100 ppm NO in N₂ at 35°C. The analysis was carried out using 0.2 mL of the sample with 30 mL/min flow of the carrier gas (helium) and the thermal conductivity detector set at high sensitivity. The column was operated at a temperature of 30°C. Operation of the detector at 165°C assured its optimum performance. Sample chromatograms showing the analysis of nitric oxide in the presence and absence of oxygen are shown in Figure 4.1. The detection limit for nitric oxide was 50 ppm based on the highest sensitivity of the chromatograph. Details of various other parameters used in the gas chromatographic analysis are given in Appendix B.
Figure 4.1 Typical Chromatogram Obtained From Gas Chromatographic Analysis of Nitric Oxide

[Operating conditions: Carrier gas flow, 30 mLs/min; Detector, Thermal conductivity detector (TCD); Detector sensitivity, High; Oven temperature, 30°C; Detector temperature, 165°C]

[Peak identifications: N₂, Retention time 1.130 min; NO, Retention time 2.613 min]
Phase 2: Preparation of char and activated carbon from lignite and their characterization

The major adsorbent preparation variables were carbonization temperature, carbonization holding time, activation temperature and time, and activation agent. Development of the microstructure was evaluated by physical characterization of the adsorbents at each stage of the preparation in order to optimize carbonization and activation process variables to obtain adsorbents with the "right" characteristics for the removal of $\text{SO}_2$.

A detailed study of $\text{SO}_2$ adsorption on lignite, chars and activated carbons was also conducted. The major operating variables were adsorbent particle size, adsorption temperature, influent $\text{SO}_2$ concentration and residence time. Adsorption characteristics and microstructure of lignite were compared with those of lignite-derived chars and activated carbons. An attempt was also made to correlate adsorption characteristics of the adsorbents with their physical characteristics. The effects of these independent variables were evaluated by a statistical design of experiments as well as by generating experimental breakthrough curves. Details are discussed below.

4.2.1 Adsorption of sulfur dioxide by lignite

In the literature, adsorption characteristics of adsorbents as well as adsorber performance have been evaluated in terms of breakthrough time, rate of adsorption and nature of adsorption equilibrium using experimental breakthrough curves (Slejko, 1988). However, since for practical reasons most of the adsorption processes are not run at equilibrium, only the breakthrough time and mid-point slope (which is related to the rate of adsorption) of the experimental breakthrough curves were considered in this work. The values of these parameters, obtained at various operating conditions are given in Table 4.2. The amount of sulfur dioxide adsorbed as well as the breakthrough times, given in Table 4.2, are those which corresponded to an effluent
### Table 4.2 Sulfur Dioxide Breakthrough Time and Mid-point Slope on Lignite As a Function of Particle Size, Adsorption Temperature, Influent Sulfur Dioxide Concentration and Residence Time

<table>
<thead>
<tr>
<th>Size, mm</th>
<th>Adsorption temperature, °C</th>
<th>Influent SO₂ concentration, ppm SO₂</th>
<th>Residence time, sec.</th>
<th>Breakthrough time, min.</th>
<th>Mid-point slope, 1/min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>75</td>
<td>3000</td>
<td>7</td>
<td>42.5</td>
<td>0.0140</td>
</tr>
<tr>
<td>5.6</td>
<td>75</td>
<td>3000</td>
<td>7</td>
<td>33.1</td>
<td>0.0400</td>
</tr>
<tr>
<td>2.0</td>
<td>175</td>
<td>3000</td>
<td>7</td>
<td>40.0</td>
<td>0.0205</td>
</tr>
<tr>
<td>5.6</td>
<td>175</td>
<td>3000</td>
<td>7</td>
<td>30.9</td>
<td>0.0511</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>1000</td>
<td>4</td>
<td>15.6</td>
<td>0.0389</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>5000</td>
<td>4</td>
<td>10.7</td>
<td>0.0608</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>1000</td>
<td>10</td>
<td>81.9</td>
<td>0.0103</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>5000</td>
<td>10</td>
<td>53.3</td>
<td>0.0187</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>30.9</td>
<td>0.0275</td>
</tr>
<tr>
<td>2.0</td>
<td>125</td>
<td>3000</td>
<td>4</td>
<td>16.6</td>
<td>0.0400</td>
</tr>
<tr>
<td>5.6</td>
<td>125</td>
<td>3000</td>
<td>4</td>
<td>16.6</td>
<td>0.0549</td>
</tr>
<tr>
<td>2.0</td>
<td>125</td>
<td>3000</td>
<td>10</td>
<td>60.8</td>
<td>0.0079</td>
</tr>
<tr>
<td>5.6</td>
<td>125</td>
<td>3000</td>
<td>10</td>
<td>34.7</td>
<td>0.0160</td>
</tr>
<tr>
<td>3.4</td>
<td>75</td>
<td>3000</td>
<td>7</td>
<td>30.6</td>
<td>0.0263</td>
</tr>
<tr>
<td>3.4</td>
<td>175</td>
<td>3000</td>
<td>7</td>
<td>23.3</td>
<td>0.0291</td>
</tr>
<tr>
<td>3.4</td>
<td>75</td>
<td>3000</td>
<td>7</td>
<td>26.0</td>
<td>0.0355</td>
</tr>
<tr>
<td>3.4</td>
<td>175</td>
<td>3000</td>
<td>7</td>
<td>22.5</td>
<td>0.0426</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>24.2</td>
<td>0.0302</td>
</tr>
<tr>
<td>3.4</td>
<td>75</td>
<td>1000</td>
<td>4</td>
<td>16.6</td>
<td>0.0533</td>
</tr>
<tr>
<td>3.4</td>
<td>175</td>
<td>1000</td>
<td>4</td>
<td>11.3</td>
<td>0.0654</td>
</tr>
<tr>
<td>3.4</td>
<td>75</td>
<td>5000</td>
<td>10</td>
<td>21.4</td>
<td>0.0160</td>
</tr>
<tr>
<td>3.4</td>
<td>175</td>
<td>5000</td>
<td>10</td>
<td>22.6</td>
<td>0.0267</td>
</tr>
<tr>
<td>2.0</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>26.3</td>
<td>0.0163</td>
</tr>
<tr>
<td>5.6</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>28.7</td>
<td>0.0240</td>
</tr>
<tr>
<td>2.0</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>30.0</td>
<td>0.0220</td>
</tr>
<tr>
<td>5.0</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>22.5</td>
<td>0.0421</td>
</tr>
<tr>
<td>3.4</td>
<td>125</td>
<td>3000</td>
<td>7</td>
<td>27.5</td>
<td>0.0289</td>
</tr>
</tbody>
</table>
sulfur dioxide concentration of 100 ppm. The selection of 100 ppm as the breakthrough concentration of sulfur dioxide was based on the detection limit of the gas chromatograph which was used to measure effluent gas composition.

4.2.1.1 Effect of residence time

Residence time is one of the most important parameters which should be considered in the design of an adsorber and the selection of adsorbents. Residence time gives an estimate of the volume of gas that can be treated within a specified time and also of the volume of the adsorbent needed for achieving the required separation. In the literature, typical residence times that have been used for carbon based adsorbents lie in the range of 4 sec (Richter, 1990). In our study, residence times of 4 to 10 sec have been used.

Adsorption experiments, used to determine the sulfur dioxide adsorption capacity of lignite, used the following operating conditions: particle size, 2-5.6 mm; adsorption temperature, 75-175°C; influent sulfur dioxide concentration, 1000-5000 ppm; residence time, 4-10 sec; flow rate, 40-100 mLs/min; mass of lignite, 1 g; diameter of the adsorber, 1.27 cm and height of the adsorbent bed, 5.5 cm.

The effects of particle size, adsorption temperature, influent sulfur dioxide concentration and residence time on sulfur dioxide breakthrough time and mid-point slope (which is related to the rate of adsorption) are shown in Table 4.2. The typical effect of residence time on breakthrough profile of sulfur dioxide through a bed of lignite is also shown in Figure 4.2. Operating conditions were: sulfur dioxide influent concentration, 5000 ppm; adsorption temperature, 125°C; and particle size, 3.4 mm.

It can be seen from the figure as well as from Table 4.2 that a shorter residence time of 4 sec resulted in an early breakthrough of sulfur dioxide (10.7 min) and a very sharp (higher mid-point slope) breakthrough profile (mid-point slope of 0.0608 min⁻¹). On the other hand, a residence time of 10 sec resulted in delayed breakthrough (81.9 min) of sulfur dioxide and a diffused sulfur dioxide breakthrough profile (mid-point slope of 0.0103 min⁻¹). The increase in the breakthrough time with
Figure 4.2 Effect of Residence Time on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite

[Operating conditions: Amount of coal, 1g; Volume of adsorber, 6.697 cc; Bed height, 5.5 cm; Flow distributor bed height, 4 cm; Particle size, 3.4 mm; Adsorption temperature, 125°C; Influent SO₂ concentration, 5000 ppm]
the increase in residence time was more prominent in the cases where influent sulfur
dioxide concentrations were low (1000 ppm) and particle sizes small (2 mm). For
example, in the case of small particle size, sulfur dioxide breakthrough time and mid-
point slope of 60.8 min and 0.0079 min⁻¹, respectively, was obtained when the
operating conditions used were: particle size, 2 mm; adsorption temperature, 125°C;
influent sulfur dioxide concentration, 3000 ppm and residence time, 10 sec (Table
4.2).

Figure 4.2 also shows that an increase in residence time resulted in a decrease
in the mid-point slope. Generally, while short residence time leads to an early leakage
of sulfur dioxide, a long time is required to achieve complete breakthrough.
Consequently, the slopes for such breakthrough curves are not steep. In the
literature, this phenomenon has been attributed to the deviation from ideal plug flow
due to axial dispersion. Contrary to the above observation, sulfur dioxide adsorption
on lignite showed different characteristics. Even though long residence time (low
empty bed space velocity) resulted in a diffused breakthrough profile of sulfur
dioxide, the breakthrough time was also long. Therefore, the diffused breakthrough
profile of sulfur dioxide as obtained for long residence time was not due to axial
dispersion. This phenomenon was attributed to the external mass transfer as the rate-
controlling mechanism for sulfur dioxide adsorption. Our result was consistent with
those obtained from a packed bed, laminar flow, gas-solid contacting system by Wilke
and Hougen (1945). These authors showed that mass transfer coefficients increased
with the increase in velocity (decrease in residence time).

4.2.1.2 Effect of influent sulfur dioxide concentration

Though the concentration of sulfur dioxide in the flue gas from power plants
depends on the type of coal used for generating power, in most of the cases, power
plant flue gases contain 1000 to 5000 ppm of sulfur dioxide. Consequently, an
influent sulfur dioxide concentration of 1000 to 5000 ppm was used in this study to
find out the effect of sulfur dioxide concentration on its removal by lignite.
The typical effect of the variation of the feed concentration on the sulfur dioxide breakthrough behavior on lignite is presented in Figure 4.3. In general, it was observed that the sulfur dioxide breakthrough time in the case of higher influent sulfur dioxide concentration was smaller than the one obtained with lower influent sulfur dioxide concentration. Also, the shape (mid-point slopes) of the sulfur dioxide breakthrough curve was steeper than the one obtained with lower influent sulfur dioxide concentration. These two phenomenon could be explained as follows: for a linear adsorption isotherm, the change in the equilibrium amount of sulfur dioxide adsorbed with change in the influent sulfur dioxide concentration \((dq/dC)\) is constant and therefore the breakthrough time will not be affected by a change in the influent sulfur dioxide concentration. However, in this work, the adsorption isotherm was assumed to be a favorable non-linear type. Consequently, \(dq/dC\) decreased as the influent concentration increased, thus resulting in the shorter sulfur dioxide breakthrough time.

It can also be seen from Figure 4.3 that in the case of low sulfur dioxide concentration (1000 ppm), the shape of the breakthrough curve was diffused. As was mentioned earlier the diffused nature was not due to the axial dispersion but to the existence of a different type of adsorption behavior of sulfur dioxide on lignite at low influent sulfur dioxide concentration.

4.2.1.3 Effect of adsorption temperature

One of the important parameters in the conceptual design of an adsorber and adsorbent is the adsorption temperature. Generally, power plant flue gas temperatures are in the range of 125-150°C. In this study, we have used three adsorption temperatures: 75, 125 and 175°C.

The typical effect on breakthrough time and mid-point slope of the breakthrough curve with adsorption temperature is given in Figure 4.4. This Figure shows that higher adsorption temperature \(175^\circ C\) resulted in a shorter sulfur dioxide breakthrough time as well as a sharper sulfur dioxide breakthrough profiles as
Figure 4.3 Effect of Influent Sulfur Dioxide Concentration on Its Breakthrough Profile in a Bed of Lignite

[Operating conditions: Amount of coal, 1g; Residence time, 7 sec; Volume of adsorber, 6.697 cc; Bed height, 5.5 cm; Flow distributor bed height, 4 cm; Particle size, 2 mm; Adsorption temperature, 125°C]
Figure 4.4 Effect of Adsorption Temperature on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite

[Operating conditions: Amount of coal, 1g; Residence time, 7 sec; Volume of adsorber, 6.697 cc; Bed height, 5.5 cm; Flow distributor bed height, 4 cm; Particle size, 5.6 mm; Influent SO$_2$ concentration, 3000 ppm]
compared to the one where a lower adsorption temperature (75°C) was used. However, comparison of Figure 4.2, 4.3 and 4.4, which show the effects of the residence time, influent sulfur dioxide concentration and adsorption temperatures, respectively, reveals that the effect of adsorption temperature on the breakthrough curves was not as pronounced as the effects of residence time and influent sulfur dioxide concentration. This phenomenon was explained on the basis of the typical counteracting effects of the adsorption temperature on the adsorption process. The rate of adsorption usually increases with an increase in adsorption temperature because of the increased rate of diffusion of the adsorbate molecules through the adsorbent. It is also known that adsorption capacity decreases with adsorption temperature. These two counteracting phenomenon nullified the effect of adsorption temperature.

4.2.1.4 Effect of lignite particle size

The typical variation of sulfur dioxide adsorption characteristics with particle size is shown in Figure 4.5. It can be seen that increasing particle size resulted in a sharpening of the breakthrough curve and a shortening of the breakthrough time. This means that short breakthrough times and large mid-point slopes of the breakthrough curves would result from large particle size. However, the impact of lignite particle size was smaller as compared to the impact of residence time and influent sulfur dioxide concentration, which will also be discussed in Section 4.2.1.5. There was an indication (Section 4.2.1.1) that the external mass transfer may be the rate-controlling mechanism for sulfur dioxide adsorption on lignite. The small impact of particle size on sulfur dioxide adsorption by lignite supported the assumption that the adsorption phenomenon was being controlled primarily by mass transfer.

4.2.1.5 Statistical design and modeling of sulfur dioxide adsorption by lignite

An experimental design that permits the test of a large number of variables using a minimum number of experiments was developed using the statistical design of
Figure 4.5 Effect of Particle Size on Sulfur Dioxide Breakthrough Profile in a Bed of Lignite

[Operating conditions: Amount of coal, 1g; Residence time, 7 sec; Volume of adsorber, 6.697 cc; Bed height, 5.5 cm; Flow distributor bed height, 4 cm; Adsorption temperature 75°C; Influent SO$_2$ concentration, 3000 ppm]
Box and Behnken (1960). In the case of experiments involving sulfur dioxide adsorption on lignite, the statistical design used a second degree graduating polynomial to fit the experimental results by the method of least squares. From the results obtained from sulfur dioxide adsorption experiments with lignite, operating conditions for subsequent adsorption experiments with other adsorbents were selected. Therefore, a simple factorial design was used in subsequent adsorption experiments involving chars and activated carbons in order to evaluate the effect of various independent variables.

The use of the second degree graduating polynomial in the case of sulfur dioxide adsorption on lignite, resulted in two equations for the breakthrough time ($Y_1$) and mid-point slope ($Y_2$) which are given as Equations 4.1 and 4.2, respectively. In these equations, $X_a$ is the coded value of the variable, i.e., +1, 0 or -1. While -1 and +1 stood for the lowest and the highest value of the variable, respectively, 0 stood for the mean value of the variable. For example, in the case of adsorption temperature, +1, 0 and -1 stood for 175, 125 and 75°C, respectively. The positive and the negative signs for the coefficients (which are the estimates of the effects of different independent variables) indicated the positive and negative effects of the corresponding variable.

$$Y_1 = 27.53 + (-4.225X_1 - 1.550X_2 - 3.608X_3 + 15.617X_4) + (4.096X_1^2 - 3.642X_2^2 + 2.546X_3^2 + 1.633X_4^2) + (0.075X_1X_2 - 2.725X_1X_3 - 6.525X_1X_4 + 1.2X_2X_3 + 1.625X_2X_4 - 5.950X_3X_4)$$  \hspace{1cm} (4.1)

$$Y_2 = 0.0289 + (0.0081X_1 + 0.0042X_2 + 0.0868X_3 - 0.2177X_4) + (-0.0022X_1^2 + 0.0055X_2^2 + 0.3768X_3^2 + 0.4089X_4^2) + (0.0011X_1X_2 + 0.0006X_1X_3 - 0.0017X_1X_4 + 0.0011X_2X_3 - 0.0003X_2X_4 - 0.0034X_3X_4)$$  \hspace{1cm} (4.2)
In Equations 4.1 and 4.2 the following independent variables were used:

\[ X_1: \] lignite particle size,
\[ X_2: \] adsorption temperature,
\[ X_3: \] influent sulfur dioxide concentration, and
\[ X_4: \] residence time.

These equations show that breakthrough time, \( Y_1 \) and mid-point slope, \( Y_2 \) of the breakthrough curve were affected by all four independent variables selected for the study. However, the magnitude of the coefficients for the various independent variables (estimates) show that residence time had the strongest effect on the breakthrough time of sulfur dioxide. While both residence time and influent sulfur dioxide concentration exerted strong influences on the mid-point slope of the sulfur dioxide breakthrough curves on lignite, residence time was again found to be the most significant variable. In comparison to residence time and influent sulfur dioxide concentration, particle size and adsorption temperature exerted little influence.

It can be seen from these statistical models (Equations 4.1 and 4.2) that all the independent variables were interactive. In the case of the statistical model equation for the breakthrough time, interaction between residence time and influent sulfur dioxide concentration and between particle size and residence time were most significant. In the case of mid-point slope, the interaction between influent sulfur dioxide concentration and residence time was the most significant. These results from statistical analysis confirmed our earlier experimental observation for the significant and the interacting variables.

4.2.1.6 Selection of operating variables for subsequent sulfur dioxide adsorption experiments

From Figures 4.2, 4.3, 4.4 and 4.5, showing the effects of residence time, influent sulfur dioxide concentration, adsorption temperature and particle size, respectively, it can be seen that low influent sulfur dioxide concentration, long residence time (low gas velocity) and smaller particle size resulted in more diffused
breakthrough profiles. In the literature, the shape of the breakthrough curve has been related to the adsorption kinetics (Ruthven, 1984). As the intention of this phase of work was to compare the sulfur dioxide adsorption capacities of char and activated carbon with that of lignite, an attempt was made to obtain constant-profile breakthrough curves of sulfur dioxide over all the adsorbents. In order to obtain constant profile sulfur dioxide breakthrough curves, the following operating conditions were selected for subsequent sulfur dioxide adsorption experiments with lignite-derived adsorbents:

<table>
<thead>
<tr>
<th>Adsorbent particle size</th>
<th>4 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption temperature</td>
<td>125°C</td>
</tr>
<tr>
<td>Influent sulfur dioxide conc.</td>
<td>3000-5000 ppm</td>
</tr>
<tr>
<td>Residence time</td>
<td>4-7 sec.</td>
</tr>
</tbody>
</table>

4.2.2 Carbonization of lignite and physical characteristics of chars

In the literature, the unique adsorption capacity of carbon-based adsorbents has been attributed to their microporosity (Richter, 1990). Development of microporosity which will favor the adsorption of gases and vapors depends on the carbonaceous precursors as well as the preparation methods. Details concerning various preparation methods have been well documented in the literature (Hassler, 1974). It has been noted that preparation methods are but various combinations of two basic processes, namely, carbonization and activation. However, the interrelationship between the preparation variables and development of microporosity as well as the relationship between microporosity and adsorption characteristics are not clearly understood. In this situation, development of an adsorbent from lignite which will exhibit the highest possible adsorption capacity was difficult. The objective of this phase of the work was to prepare various adsorbents such as char and activated carbons from lignite. For this purpose, lignite coal was subjected to carbonization in order to prepare chars which were subsequently activated for the preparation of activated carbons. In addition, chars and activated carbons were
thoroughly characterized and subsequently subjected to adsorption experiments. This section will focus on the development of physical characteristics such as micropore surface area, volume, pore size and its distribution due to carbonization of lignite.

Except under conditions of extremely rapid heating and high temperatures, carbonization or thermal decomposition is the first step through which coal particles undergo major physical and chemical changes. The thermal decomposition of the carbonaceous material in the absence of air or oxygen results in the formation of solids, liquids, and gaseous products. In the carbonization process, the principle product is char, which as a result of the incomplete nature of the carbonization process (because carbonization does not result in complete burn-off of carbon material), retains much of the structure, complexity, and signature of the raw material undergoing carbonization.

Carbonization temperature, holding time (time at the steady final carbonization temperature), heating rate and inert gas flow rate are important variables which affect the quality of the final product char. To maximize the yield of char, a combination of slow heating rate (<1°C/sec) with low temperature carbonization (carbonization temperature ca. 500°C) has been recommended in the literature as higher carbonization temperatures have been found to cause rupture of the aromatic rings resulting in a decrease of microporosity.

In this work, heating rate, inert gas type and inert gas flow rate were kept constant in all the carbonization experiments. Nitrogen gas (flow rate of 100 mL/min) was used as the inert gas. Only carbonization temperature and holding time were selected as the independent variables.

All the results obtained from carbonization experiments were for dry (as-received) lignite in the particle size range of -5.6 +4.75 mm. Yields of gaseous products were calculated on a nitrogen-free basis from the gas composition, volume of the gas produced, and the amount of lignite used. In all figures, the total yields of any product are given in the ordinate as a weight per cent of the lignite. Component mass balances were not possible because, of the total volatile matter produced, only
C$_1$-C$_6$ hydrocarbons, CO and CO$_2$ were directly determined. This left a considerable quantity of products unaccounted for which consisted mainly of tar and water, as well as volatile organic materials lost during tar recovery.

The effect of carbonization temperature and holding time on the development of physical characteristics as well as formation of various products are discussed below.

4.2.2.1 Effect of carbonization temperature on gas, char, and tar gas yields

Figure 4.6 shows the yields of gas, char and tar obtained from carbonization of lignite at temperatures ranging from 350 and 550°C. It can be seen from Figure 4.6 that the tar yield were 5.0, 11.0, 10.2 and 8.4% for carbonization temperatures of 350, 410, 475 and 550°C, respectively. The decrease in the yield of tar due to an increase in the carbonization temperature from 475 to 550°C was attributed to the onset of secondary decomposition of tar vapor at higher temperature.

It also can be seen from Figure 4.6 that while the gas yields increased continuously from 16.1 to 20.1 to 25.4 to 29.7% with increases in temperature from 350 to 410 to 475 to 550°C, respectively, char yields decreased continuously from 78.9 to 68.9 to 64.4 to 61.9%, respectively. These results followed typical trends of gas, tar and char yields that are obtained from any carbonization experiment.

Similar trends in product distribution have also been observed by Winer (1958) during his studies on low temperature carbonization (500°C) assays of Saskatchewan lignite.

4.2.2.2 Effect of temperature on CO$_2$, CO and H$_2$ yields

The thermal decomposition of coal depends on the nature of the coal as well as the carbonization temperature. In the literature, the evolution of various gaseous products due to carbonization have been linked to different reactions such as decarboxylation, dealkylation, and aromatic ring rupture. As mentioned earlier, the principle product in our work was char which generally has more porosity due to an
Figure 4.6 Effect of Carbonization Temperature on Char, Tar and Gas Yields From Lignite Coal

[Operating conditions: Carrier gas, N₂; Flow rate, 100 mL./min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min]
increase in aromaticity compared to the parent coal. Therefore, evaluation of the gaseous products formed due to carbonization was important. Furthermore, it was also worthwhile to find out the approximate make-up of the gaseous product in order to evaluate its calorific value.

The yields of hydrogen and principal oxygenated species such as carbon dioxide and carbon monoxide are shown in Figure 4.7. It can be seen that the formation of carbon dioxide and carbon monoxide increased monotonically with an increase in carbonization temperature. At a carbonization temperature of 550°C, yields of CO and CO₂ were 1.7 and 13.9%, respectively. On the other hand, hydrogen yields increased from 0.0 to 0.06 to 0.19 to 0.58% with increases in carbonization temperature from 350 to 410 to 475 to 550°C, respectively.

Figure 4.7 also shows that carbon monoxide and hydrogen did not form at 350°C; these two components evolved at higher temperatures and increased continuously thereafter with an increase in the carbonization temperature. On the contrary, tar (Fig. 4.6), and carbon dioxide (Fig. 4.7) evolved at temperatures as low as 350°C and the ultimate yield did not seem to depend significantly on the carbonization temperature.

In the literature, formation of carbon dioxide during carbonization has been attributed to the decomposition of acid, ester and ether functional groups. However, while decomposition of acidic functional groups take place at lower carbonization temperatures, decomposition of the ester and ether functionalities require higher carbonization temperatures in the range of 700°C. Therefore, formation of carbon dioxide at low temperatures has been attributed to the decomposition of acidic functionalities.

The formation of carbon monoxide at carbonization temperatures lower that 500°C has been attributed to the cleavage of carbonyl groups and ether linkages. In this work, formation of carbon monoxide during carbonization of lignite was negligible at carbonization temperatures up to 410°C. It can be seen from Figure 4.7 that though formation of carbon monoxide was negligible up to a carbonization
Figure 4.7 Effect of Carbonization Temperature on the Yield of Non-hydrocarbon Gases Such As CO, CO$_2$ and H$_2$ From Lignite Coal

[Operating conditions: Carrier gas, N$_2$; Flow rate, 100 mL /min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min]
temperature of 410°C, significant production of carbon monoxide was achieved at higher carbonization temperatures (1.7% at 550°C). As mentioned earlier, decomposition of ketone and ether functionalities require high carbonization temperatures. Therefore, the low yield of carbon monoxide obtained at low carbonization temperatures was consistent with the assumption that carbon monoxide was formed during the decomposition of ketone and ether functionalities.

Though production of hydrogen increased monotonically with the increase in carbonization temperature, the percentage of hydrogen in the gaseous product was negligible. In the literature, formation of hydrogen during carbonization has been attributed to the aromatic ring rupture. Therefore, in the range of carbonization temperature used in this study, the rupture of aromatic ring would be negligible.

4.2.2.3 Effect of temperature on hydrocarbon yields

The variations of the C₁-C₆ hydrocarbon yields with temperature are shown in Figure 4.8. It can be seen that the yield of methane increased steadily with temperature from 1.9% at 350°C to 9.2% at 550°C. C₂ to C₃ yields, on the other hand, increased with increase in carbonization temperature up to 475°C, then decreased with further increase in carbonization temperature to 550°C. C₆ hydrocarbon yields increased continuously over the temperature range. However, the formation of C₂-C₆ hydrocarbons were not very significant which was consistent with other results reported in the literature (Benjamin et. al., 1978). In the literature, formation of methane and ethane during low temperature carbonization have been attributed to alkylation reactions (Benjamin et. al., 1978). Methane can also be formed along with carbon dioxide due to alkylation followed by decarboxylation reactions as follows:

\[
\text{CH}_3\text{COOH} = \text{CH}_4 + \text{CO}_2
\]  

(5.3)
Figure 4.8 Effect of Carbonization Temperature on the Yields of Hydrocarbon Gases From Lignite Coal

[Operating conditions: Carrier gas, N$_2$; Flow rate, 100 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min]
Therefore, the continuous increase in methane production was consistent when viewed along with increased production of carbon dioxide as discussed in the previous section.

The product gas composition indicated that carbonization resulted in the formation of a gas mixture which contained appreciable quantities of methane and other light hydrocarbons and therefore could be used as an medium energy fuel.

4.2.2.4 The effect of carbonization temperature on physical properties of chars

It has already been mentioned that the objective of this part of the work was to prepare an efficient adsorbent from lignite using optimum preparation variables which will extract the best out of the raw material. In the literature, the adsorption of gases has been attributed to the microporosity of the carbon based adsorbents (Mahajan, 1984). Therefore, assessment of the microporosity was very important. As mentioned earlier, in order to assess microporosity, one should know micropore surface area, micropore volume, median pore diameter and pore size distribution present in the adsorbent. Micropore surface area and micropore volume indicate the accessible portion of the adsorbent or the catalyst. Median pore diameter, on the other hand, gives an idea about the average size of the pores which when coupled with the pore size distribution, indicates the proportion of pores of different sizes. The changes in the physical properties due to carbonization temperature are presented in Table 4.3.

Micropore surface area:

Micropore surface area implies the accessible surface present in the adsorbent which can be exploited for the adsorption of gases and vapors. The changes in the micropore surface area with carbonization temperature are shown in Figure 4.9. It can be seen (Figure 4.9) that the micropore surface area increases from 67 to 90 to 136 m²/g with increases in carbonization temperature from 350 to 410 to 475°C (for a carbonization holding time of 120 min). However, with a further increase of
### Table 4.3  Physical Characteristics of Chars Determined From CO\textsubscript{2} Adsorption Isotherm

<table>
<thead>
<tr>
<th>Method of analysis</th>
<th>Carbonization temperature, °C</th>
<th>350</th>
<th>350</th>
<th>350</th>
<th>410</th>
<th>410</th>
<th>410</th>
<th>475</th>
<th>475</th>
<th>475</th>
<th>550</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbonization holding time, min</td>
<td>30</td>
<td>75</td>
<td>120</td>
<td>30</td>
<td>75</td>
<td>120</td>
<td>30</td>
<td>75</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Dubinin-Ashtakov:</td>
<td>Micropore surface area, m\textsuperscript{2}/g</td>
<td>25.7</td>
<td>36.6</td>
<td>67.1</td>
<td>69.4</td>
<td>77.4</td>
<td>90.5</td>
<td>109.4</td>
<td>116.5</td>
<td>136.1</td>
<td>114.3</td>
</tr>
<tr>
<td></td>
<td>Micropore volume, cc/g</td>
<td>0.0135</td>
<td>0.019</td>
<td>0.034</td>
<td>0.033</td>
<td>0.036</td>
<td>0.043</td>
<td>0.049</td>
<td>0.051</td>
<td>0.062</td>
<td>0.055</td>
</tr>
<tr>
<td>Hurvath-Kawazoe:</td>
<td>Micropore volume, cc/g</td>
<td>0.014</td>
<td>0.019</td>
<td>0.036</td>
<td>0.034</td>
<td>0.036</td>
<td>0.043</td>
<td>0.049</td>
<td>0.051</td>
<td>0.061</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>Median pore diameter, Å</td>
<td>11.0</td>
<td>10.5</td>
<td>10.1</td>
<td>8.5</td>
<td>8.2</td>
<td>7.9</td>
<td>7.3</td>
<td>6.8</td>
<td>6.8</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>Pore size distribution, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;5 Å</td>
<td>8.7</td>
<td>9.2</td>
<td>8.6</td>
<td>11.8</td>
<td>14.8</td>
<td>17.4</td>
<td>18.8</td>
<td>21.2</td>
<td>15.6</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>5 - &lt;10 Å</td>
<td>34.0</td>
<td>37.4</td>
<td>37.1</td>
<td>45.0</td>
<td>44.9</td>
<td>44.3</td>
<td>47.0</td>
<td>50.2</td>
<td>51.7</td>
<td>41.6</td>
<td></td>
</tr>
<tr>
<td>10 - &lt;15 Å</td>
<td>16.7</td>
<td>19.0</td>
<td>19.5</td>
<td>19.8</td>
<td>18.2</td>
<td>18.9</td>
<td>17.6</td>
<td>15.9</td>
<td>18.9</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>15 - &lt;20 Å</td>
<td>9.4</td>
<td>6.7</td>
<td>7.3</td>
<td>6.5</td>
<td>6.2</td>
<td>5.8</td>
<td>5.5</td>
<td>4.7</td>
<td>5.4</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>20 - &lt;25 Å</td>
<td>15.2</td>
<td>6.1</td>
<td>6.1</td>
<td>4.4</td>
<td>4.8</td>
<td>4.7</td>
<td>4.0</td>
<td>3.3</td>
<td>3.8</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>25 - &gt;25 Å</td>
<td>16.0</td>
<td>21.6</td>
<td>21.4</td>
<td>12.5</td>
<td>11.1</td>
<td>9.9</td>
<td>7.1</td>
<td>4.7</td>
<td>4.6</td>
<td>14.4</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.9 Micropore Surface Area (Estimated by Dubinin-Astakhov Method) of Chars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min

[Carbonization Operating conditions: Carrier gas, N₂; Flow rate, 100 mL /min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
carbonization temperature, the micropore surface area of chars decreased from 136 m$^2$/g at 475°C to 114 m$^2$/g at 550°C indicating an optimum carbonization temperature exists where the resulting char exhibited the highest micropore surface area.

**Micropore volume:**

It is the micropore volume within the pores of the adsorbent that enable it to adsorb large amounts of gases. Therefore, the changes in the micropore volume of lignite due to carbonization was studied. Figure 4.10 shows micropore volume of chars as a function of carbonization temperature. Micropore volumes changed from 0.034 to 0.043 to 0.062 to 0.055 cc/g with increase in carbonization temperature from 350 to 410 to 475 to 550°C. The results indicate that the micropore volume peaks around 475°C.

**Median pore diameter:**

Larger micropore surface area and micropore volume do not necessarily assure large adsorption of gases and vapors by the adsorbent. Rather, the most important parameters that should be considered are the pore size and pore size distribution because it is the pore size which allows the adsorbate of a certain size to get into the pores and subsequently adsorb onto the accessible surface.

The changes in the median pore diameter due to carbonization is shown in Figure 4.11. Median pore diameter decreased from 10.1 to 7.9 to 6.8 Å with increases in carbonization temperature from 350 to 410 to 475°C. The decrease in the median pore diameter indicated an increase in the proportion of ultramicropores in chars prepared at higher carbonization temperatures. However, with a further increase in the carbonization temperature to 550°C, the median pore diameter increased to 7.0 Å which suggested that carbonization of lignite at temperatures higher than 475°C would not result in any further increase in the proportion of ultramicroporosity. Rather, it would result in the enlarging of already existing ultramicropores.
Figure 4.10 Micropore Volume (Estimated by Dubinin-Astakhov Method) of Chars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min

[Carbonization Operating conditions: Carrier gas, N₂; Flow rate, 100 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
Figure 4.11 Median Pore Diameter (Estimated by Horvath-Kawazoe Method) of Chars Prepared at Different Carbonization Temperatures for a Carbonization Holding Time of 120 min

[Carbonization Operating conditions: Carrier gas, N\textsubscript{2}; Flow rate, 100 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO\textsubscript{2}]
Micropore size distribution

Finally, in the literature it has been mentioned that pore size distribution can describe the adsorbent in more details than any other physical characteristics (Mahajan, 1984). The comparison of the micropore size distribution between lignite and chars is shown in Figure 4.12. It can be seen that chars have a larger proportion of micropores in the range between 5 to 8 Å in comparison to that of lignite.

When the information on micropore surface area, micropore volume, and median pore diameter was coupled with micropore size distribution, it was inferred that the increase in micropore surface area, micropore volume and decrease in median pore diameter due to carbonization process were primarily because of the opening of numerous ultramicropores (<10 Å) in the lignite structure due to carbonization.

4.2.2.5 Effect of carbonization holding time on gas, char and tar yields

Carbonization holding time was another important parameter studied in this work. Figure 4.13 shows the yields of gas, char and tar yields obtained in carbonizing lignite over the carbonization holding time range varying between 30 and 120 min. The tar yield changed from 5.5 to 8.0 to 11.0% due increases in carbonization holding time from 30 to 75 to 120 min, respectively, (carbonization temperature of 410°C) while gas yields increased from 17.8 to 18.9 to 20.1%. At a carbonization temperature of 410°C, char yield decreased from 76.7 to 73.1 to 68.9% due to increases in carbonization holding time from 30 to 75 to 120 min, respectively. Similar trends in the tar, gas and char yield were also observed at other carbonization temperatures.

With the increase in the carbonization holding time, the yield of tar and the gaseous products increased at the expense of the char which decreased continuously with the increase in carbonization holding time.
Figure 4.12 Comparison of Micropore Size Distribution of Chars Prepared at Different Carbonization Temperatures With That of Lignite (Points for the Char, Prepared at 475°C, and that for Lignite Are Connected by Solid Lines)

[Carbonization Operating conditions: Carrier gas, N₂; Flow rate, 100 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
Figure 4.13 Effect of Carbonization Holding Time on the Yields of Char, Tar and Gas From Lignite Coal

[Carbonization Operating conditions: Carrier gas, N₂; Flow rate, 100 mL 'min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 410°C; Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
4.2.2.6 Effect of carbonization holding time on hydrocarbon yields

The variations of the C\textsubscript{1}-C\textsubscript{6} hydrocarbon yields with carbonization holding time are shown in Figure 4.14. The yield of methane increased steadily with time from 2.9% at 30 min to 4.5% at 120 min. But, the yield of C\textsubscript{3} to C\textsubscript{4} passed through an optima around 75 min. C\textsubscript{2} hydrocarbon yield increased continuously from 1.3 to 1.4 to 1.7% with increases in the carbonization holding time from 30 to 75 to 120 min, respectively.

Though, the yields of C\textsubscript{3} to C\textsubscript{6} hydrocarbons went through a maxima, total yields of C\textsubscript{1}+C\textsubscript{2} hydrocarbons increased continuously over the carbonization holding time range studied.

4.2.2.7 Effect of carbonization holding time on the physical properties of chars

Table 4.3 shows the physical properties of chars prepared at different combinations of carbonization temperature and holding time.

For any level of carbonization temperature, micropore surface area and micropore volume increased continuously with increase in carbonization holding time. Although the median pore diameter decreased monotonically with increases in the carbonization holding time for carbonization temperatures up to 410°C, at a carbonization temperature of 475°C, the median pore diameter decreased from 7.3 to 6.8 to 6.8 Å with increases in carbonization holding time from 30 to 75 to 120 min, respectively. This indicated that at a carbonization temperature of 475°C, generation of ultramicropores reached a maximum around a carbonization holding time of 120 min. Therefore, it was assumed that a further increase in carbonization holding time or carbonization temperature might result in an increase in median pore diameter indicating the commencement of micropore destruction. However, it was not conclusive from the results obtained from physical characterization of chars prepared at carbonization holding times ranging from 30 to 120 min.
Figure 4.14 Effect of Carbonization Holding Time on the Yields of Hydrocarbon Gases From Lignite Coal

[Carbonization Operating conditions: Carrier gas, N₂; Flow rate, 100 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 410°C; Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
4.2.2.8 Optimization of carbonization parameters

The micropore surface area (Fig. 4.9), micropore volume (Fig. 4.10) of chars increased with increase in carbonization temperature up to 475°C, went through a maxima and then again decreased at a carbonization temperature of 550°C, though the carbon burn-off increased continuously from 350 to 550°C. A similar trend, i.e., presence of an optimum temperature, has also been observed for median pore diameter (Fig. 4.11). Therefore, an optimum carbonization temperature did exist where the chars exhibited the highest micropore surface area, micropore volume and smallest median pore diameter, i.e., highest microporosity. The micropore size distributions also supported this inference. It can be seen from Figure 4.12, which shows micropore size distribution of chars, that chars prepared at a carbonization temperature of 475°C contained larger proportions of microporosity in comparison to the chars prepared at other temperatures, i.e., 350, 410 and 550°C.

It can also be seen from Table 4.3 that in the case of carbonization temperatures up to 475°C, all the physical characteristics changed continuously. Therefore, there was no optimum carbonization holding time within the range studied. However, it is seen from Table 4.3 that the median pore diameter of chars, prepared at 475°C, leveled off at 6.8Å after a carbonization holding time of 75 min. This phenomenon indicates that the development of microporosity levels off at around a carbonization holding time of 120 min.

Similar results have been obtained by Nandi et. al. (1964) when they measured the changes in the pore volume and surface area of three anthracites upon carbonization at different final temperatures with heating rates of 5°C/min. They also have observed the presence of an optimum carbonization temperature which is around 600°C.

This phenomena may have resulted due to two competing processes. Thermal bond breaking produced tar and other volatile matters, the removal of which increased the micropore volume and widened constrictions, resulting in a large increase in the micropore surface area. Bond breaking also facilitates the alignment
and coalescence of the coal's structural units tending to decrease the micropore volume and micropore surface area. At the same time, bond formation or crosslinking results in decreased micropore volume and surface area. The balance of these two competing processes depends on the rank of the coal (content of volatile matter), heating rate, maximum temperature and holding time at maximum temperature. In the literature, similar phenomena, i.e., decrease in micropore surface area and micropore volume at higher temperature, has been attributed to the resolidification and shrinkage of char particles (Lu and Do, 1991).

4.2.3 Sulfur dioxide adsorption by chars

Thorough physical characterization of chars produced under different conditions has enabled us to find out the char with highest microporosity, and in the literature, the adsorption capacity of adsorbents has been attributed to their porosity. Therefore, it was decided to determine whether or not the best adsorbent (based on the physical characteristics) would exhibit the highest sulfur dioxide adsorption capacity.

Adsorption experiments, carried out to test sulfur dioxide adsorption capacities of the lignite-derived chars, used the following operating conditions: adsorption temperature, 125°C; residence time, 4 sec; influent sulfur dioxide concentration, 5000 ppm; and particle size, 4 mm.

Figure 4.15 shows the variation in sulfur dioxide adsorption capacity, which corresponds to the amount of sulfur dioxide adsorbed by one gram of the adsorbent over the time period studied, as a function of carbonization temperature. Sulfur dioxide adsorption capacity of chars increased from 0.016 to 0.018 to 0.022 g/g of char with increases in the carbonization temperature from 375 to 410 to 475°C, respectively, and then decreased to 0.019 g/g of char with further increase in the carbonization temperature to 550°C. Thus, char prepared at 475°C exhibited the maximum sulfur dioxide adsorption capacity.
Figure 4.15 Effect of Carbonization Temperature (Carbonization Holding Time of 120 min) on the Sulfur Dioxide Adsorption Capacity of Char

[Test conditions: Influent gas composition, 5000 ppm SO$_2$; Bed height, 5.5 cm; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of char, 1 g]
The sulfur dioxide breakthrough profiles for chars and lignite are shown in Figure 4.16. Comparison of the two profiles shows that there are no significant differences in the shape of the breakthrough profiles for sulfur dioxide on lignite and chars indicating that the rate controlling mechanisms for sulfur dioxide adsorption on the two different types of adsorbents (lignite and char) were similar under the operating conditions used.

The changes in the physical characteristics of chars as a result of carbonization have been discussed in detail in Section 4.2.3.4. Table 4.3 summarizes the physical properties for various chars. It can be seen from Table 4.3 that the micropore volume and micropore surface area went through an optima around 475°C. An important observation was that maximum sulfur dioxide adsorption capacity was also exhibited by the char prepared at a carbonization temperature of 475°C. Therefore, there was a close agreement between the microporosity, such as micropore surface area, volume, pore size and its distribution (measured from carbon dioxide adsorption) and the adsorption characteristics, which conclusively proves that adsorption capacity of any adsorbent is directly proportional to its microporosity. This correlation was possible because of the precise estimation of the microstructure in terms of micropore surface area, micropore volume, median pore diameter and most importantly, pore size distribution.

Chars, obtained by carbonization of lignite, exhibited higher sulfur dioxide adsorption capacity than lignite on the basis of the same amount of each adsorbent. For example, in the case of char, sulfur dioxide adsorption capacity was reported on the basis of 1 g of char. However, carbonization resulted in the loss of lignite. In order to examine any real improvement in sulfur dioxide removal efficiency of chars in comparison to that of lignite, their adsorption capacities should be evaluated on the basis of same starting mass of lignite (normalized mass). Table 4.4 shows the amount of sulfur dioxide adsorbed with respect to 1g of normalized amount of the adsorbent which took care of the carbon burn-off from lignite during carbonization. The Table shows that, on the basis of the normalized mass of each adsorbent, no significant
Figure 4.16 Comparison of the Sulfur Dioxide Breakthrough Profiles of Chars Prepared at Different Carbonization Temperatures With That of Lignite

[Test conditions: Influent gas composition, 5000 ppm SO₂; Bed height, 5.5 cm; Residence time, 4 sec; Adsorption temperature, 1250°C; Amount of char, 1 g]
Table 4.4  Sulfur Dioxide Adsorption Capacity of Lignite, Char and Activated Carbon on the Basis of 1 g of the Starting Material (Lignite)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Amount of SO$_2$ adsorbed, mg / g of adsorbent</th>
<th>Carbon Burn-off, %</th>
<th>Amount of SO$_2$ adsorbed, mg / g of lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACC, 550°C</td>
<td>49</td>
<td>36</td>
<td>31</td>
</tr>
<tr>
<td>ACC, 650°C</td>
<td>57</td>
<td>40</td>
<td>34</td>
</tr>
<tr>
<td>ACC, 750°C</td>
<td>47</td>
<td>49</td>
<td>24</td>
</tr>
<tr>
<td>ACS, 550°C</td>
<td>61</td>
<td>36</td>
<td>39</td>
</tr>
<tr>
<td>ACS, 650°C</td>
<td>68</td>
<td>43</td>
<td>40</td>
</tr>
<tr>
<td>ACS, 750°C</td>
<td>93</td>
<td>56</td>
<td>41</td>
</tr>
<tr>
<td>Char, 475°C</td>
<td>26</td>
<td>35</td>
<td>17</td>
</tr>
<tr>
<td>Lignite</td>
<td>15</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

ACC : Activated Carbon / CO$_2$;
ACS : Activated Carbon / Steam
improvement in the amount of sulfur dioxide adsorbed was achieved due to carbonization of lignite. The explanation for this phenomenon comes from our early studies on the physical characterization of the adsorbents where it was observed that carbonization resulted in the opening of numerous ultramicropores, particularly pores of size <6Å. However, under the dynamic adsorption conditions, those pores were less accessible to sulfur dioxide molecules. Therefore, despite the large improvement in the overall microporosity of lignite during carbonization, sulfur dioxide adsorption capacity of chars did not improve significantly based on the unit mass of the starting material.

4.2.4 Activation of char

In some cases chars prepared by carbonization do not have adequate adsorption capacity. In this situation, chars are generally subjected to another process which is known as activation. Activation is the controlled oxidation of carbonaceous materials using an oxidant. This results in the change in the pore characteristics of the char. It has been observed by Dutta et. al. (1977) that the change in the pore characteristics of char during activation depends on carbon burn-off and activation temperature. In the literature (Hassler, 1974), various oxidants or activation agents have been reported which include air, oxygen, carbon dioxide and steam. While the reaction of char with air and oxygen are exothermic, that of carbon dioxide and steam are endothermic. Due to the endothermic nature of the reaction between char and steam or carbon dioxide, rates of char oxidation and hence, carbon burn-off can be controlled more easily as compared to the reaction between char and air or oxygen. Therefore, for the activation of char, steam and carbon dioxide are more preferable to air and oxygen. Our early results showed that lignite-derived chars did not show much improvement in sulfur dioxide adsorption capacity, presumably due to the presence of a high percentage of ultramicropores. Therefore, char was subjected to activation in order to enlarge the already existing pores in chars. Carbon dioxide and steam were used as the activation agent in this work as endothermic activation
process offer better control of pore characteristics. Furthermore, as activation enlarges the pores of char, the starting material should be the one with the highest amount of ultramicroporosity which during the course of activation would be transformed to supermicroporosity. Our results show that chars carbonized at 475°C for 120 min exhibited the highest ultramicroporosity. Therefore, all the activation experiments were carried out with chars prepared at 475°C for 120 min.

In the activation process, the important operating parameters which were studied were temperature, time and activation agent. The effect of these operating parameters on the development of microporosity as well as sulfur dioxide adsorption characteristics will be discussed in the following sections.

4.2.4.1. Effect of activation temperature

It is known that carbonization and activation result in the improvement of porosity which is generally proportional to the carbon burn-off. However, high carbon burn-off also decreases mechanical stability of the resulting char or activated carbon adsorbents because of increased ash production. Therefore, in activation experiments, activation temperatures ranging from 550 to 750°C were used. The selection of the range of activation temperatures was based on the extent of carbon burn-off. The changes in the micropore volume, micropore surface area and pore volume distribution of different activated carbons have been summarized in Table 4.5.

Micropore surface area

The changes in the micropore surface area with activation temperature for steam and carbon dioxide activation also is shown in Figure 4.17. It can be seen from the Figure that the micropore surface area for both steam and carbon dioxide activated carbons went through an maximum around an activation temperature of 650-675°C. This suggests that the activated carbons produced at this temperature range will exhibit the highest microporosity as well.
Table 4.5  Physical Characteristics of Activated Carbons Determined From CO₂ Adsorption Isotherm

<table>
<thead>
<tr>
<th>Method of analysis</th>
<th>Activation temperature, °C</th>
<th>Activation time, min</th>
<th>550</th>
<th>650</th>
<th>750</th>
<th>550</th>
<th>650</th>
<th>750</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15 CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dubinin-Astakhov:</td>
<td></td>
<td>15 CO₂</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Micropore surface area, m²/g</td>
<td>158.4</td>
<td>219.6</td>
<td>219.2</td>
<td>153.5</td>
<td>185.5</td>
<td>182.5</td>
<td>203.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micropore volume, cc/g</td>
<td>0.071</td>
<td>0.090</td>
<td>0.099</td>
<td>0.070</td>
<td>0.085</td>
<td>0.084</td>
<td>0.097</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Horvath-Kawazoe:</td>
<td></td>
<td>15 H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micropore volume, cc/g</td>
<td>0.073</td>
<td>0.089</td>
<td>0.101</td>
<td>0.071</td>
<td>0.085</td>
<td>0.086</td>
<td>0.095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median pore diameter, Å</td>
<td>8.5</td>
<td>7.7</td>
<td>8.3</td>
<td>8.7</td>
<td>8.3</td>
<td>9.0</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore size distribution, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;4 Å</td>
<td>5.9</td>
<td>7.5</td>
<td>7.2</td>
<td>5.5</td>
<td>6.5</td>
<td>5.5</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 - &lt;5 Å</td>
<td>3.3</td>
<td>3.8</td>
<td>3.0</td>
<td>3.1</td>
<td>3.9</td>
<td>3.1</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 - &lt;6 Å</td>
<td>18.8</td>
<td>19.8</td>
<td>18.4</td>
<td>18.0</td>
<td>19.4</td>
<td>16.6</td>
<td>16.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 - &lt;10 Å</td>
<td>13.6</td>
<td>13.4</td>
<td>13.5</td>
<td>13.4</td>
<td>12.8</td>
<td>13.6</td>
<td>13.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 - &lt;20 Å</td>
<td>39.4</td>
<td>39.2</td>
<td>39.6</td>
<td>42.5</td>
<td>38.5</td>
<td>40.2</td>
<td>39.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 - &gt;20 Å</td>
<td>19.0</td>
<td>16.3</td>
<td>20.2</td>
<td>17.5</td>
<td>18.9</td>
<td>21.0</td>
<td>22.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.17 Micro pore Surface Area (Estimated by Dubinin-Astakhov Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min

[Activation operating conditions: Activation agent, CO$_2$ or steam; Flow rate, 150 mL/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 475$^\circ$C; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125$^\circ$C; Analysis temperature, 0$^\circ$C; Adsorbate, CO$_2$]
It also can be seen from Figure 4.17 that the micropore surface area of activated carbons prepared by carbon dioxide activation were higher than those obtained from steam activation. For example, micropore surface areas of activated carbons, obtained at 650°C, are 219 and 185 m²/g for carbon dioxide and steam activation, respectively.

**Micropore volume**

Table 4.5 as well as Figure 4.18 show the changes in the micropore volume of different activated carbons with activation temperature and activating agent.

It can be seen from Table 4.5 and Figure 4.18 that in the case of carbon dioxide activation, micropore volume increased continuously from 0.07 to 0.09 to 0.10 cc/g with increases in activation temperature from 550 to 650 to 750°C. In the case of steam activation, however, micropore volume reached a maximum of 0.085 cc/g at 650°C and then decreased insignificantly to 0.084 cc/g at 750°C suggesting that the process of evolution of microporosity reached its maximum around an activation temperature of 650°C.

It should be mentioned here that the results concerning micropore surface area and micropore volume are not enough to draw any conclusion concerning the desired microporosity which is required to enable the adsorbent to exhibit high adsorption capacity. Rather it is the pore size and its distribution that should be given more importance.

**Median pore diameter**

Figure 4.19 shows median pore diameters of different activated carbons. Median pore diameters of both carbon dioxide- and steam-activated carbons decreased due to an increase in activation temperature from 550 to 650°C. However, further increases in the activation temperature from 650 to 750°C, resulted in a corresponding increase in the median pore diameter. In both carbon dioxide and steam activation processes, variation in the median pore diameter showed the
Figure 4.18 Micropore Volume (Estimated by Dubinin-Astakhov Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min

[Activation operating conditions: Activation agent, CO$_2$ or steam; Flow rate, 150 mLs/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 475$^\circ$C; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125$^\circ$C; Analysis temperature, 0$^\circ$C; Adsorbate, CO$_2$]
Figure 4.19 Median Pore Diameter (Estimated by Horvath-Kawazoe Method) of Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min

[Activation operating conditions: Activation agent, CO$_2$ or steam; Flow rate, 150 mLs/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 475°C; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO$_2$]
presence of an optimum activation temperature where activated carbons exhibited a minimum median pore diameter.

**Micropore size distribution**

The results discussed in the previous sections concerning the nature of changes in the micropore surface area, micropore volume and median pore diameter indicated the presence of an optimum activation temperature for both steam and carbon dioxide activation.

In the case of steam activation, the presence of an optimum point with respect to micropore surface area, micropore volume and median pore diameter suggested that the optimum activation temperature was around 650-675°C. In the case of carbon dioxide activated carbons, micropore surface area and median pore diameter went through an optimum at an activation temperature around 650-675°C as well. However, the monotonic increase in the micropore volume in carbon dioxide activated carbons with increase in activation temperature was questionable. Therefore, more precise assessment of the microporosity of activated carbons was carried out with the help of the results concerning micropore size distribution. Micropore size distributions for carbons activated at different temperatures are given in Table 4.5, and are shown in Figures 4.20 and 4.21 for carbon dioxide and steam activation, respectively.

It can be seen from the Figure 4.20 as well as Table 4.5 that the percentage of the ultramicropores (pore size <10 Å) increased from 41.6 to 44.5 % with increase in the activation temperature from 550 to 650°C. This increase was associated with the decrease in the percentage of pores of sizes >20 Å and the percentage of supermicropores (10 < pore size < 20 Å) remained almost constant. It also can be seen that further increase in activation temperature from 650 to 750°C resulted in the transformation of micropores into mesopores. Therefore, though micropore volume of carbon dioxide activated carbons increased continuously, it can be seen that
Figure 4.20 Comparison of Micropore Size Distribution of Carbon Dioxide Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min

[Activation operating conditions: Activation agent, CO₂; Flow rate, 150 mLs/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 475°C; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
Figure 4.21 Comparison of Micropore Size Distribution of Steam Activated Carbons Prepared at Different Activation Temperatures for an Activation Time of 15 min

[Activation operating conditions: Activation agent, Steam; Flow rate, 150 mLs/min; Residence time, 1.0 min; Amount of lignite, 10 g; Carbonization temperature, 475°C; Carbonization holding time, 120 min. Analysis conditions: Degassing temperature, 125°C; Analysis temperature, 0°C; Adsorbate, CO₂]
development of microporosity reached a maximum around an activation temperature of 650°C.

It can be seen from Figure 4.21 as well as from Table 4.5 that the percentage of ultramicropores (pore size <10 Å) changed from 26.6 to 29.6 to 25.6 % with an increase in the activation temperature from 550 to 650 to 750°C. It can also be seen from the Table that the percentage of supermicropores changed from 55.9 to 51.3 to 53.8% of the total pore volume with the increases in the activation temperature from 550 to 650 to 750°C. On the other hand, percentage of transitional pores or mesopores (pores larger than 20Å) increased continuously over the activation temperature range studied. Therefore, overall microporosity (ultra and supermicropores) decreased monotonically over the range of activation temperature studied. So, even though results concerning micropore surface area, micropore volume and median pore diameter of steam activated carbons indicated the presence of an optimum in the activation temperature, micropore size distribution showed that microporosity decreased continuously with activation temperature.

4.2.4.2. Activation time

It was mentioned earlier that while changes in the pore size distribution of carbon adsorbents during activation depend on carbon burn-off, carbon burn-off depends on activation temperature and time. In order to study the effect of activation time, char was activated at three different activation times of 15, 30 and 45 min for a fixed activation temperature of 650°C. However, only physical characteristics of activated carbons prepared at 15 and 45 min are reported in Table 4.5.

It can be seen from Table 4.5 that physical characteristics of the activated carbons also were a function of activation time. The micropore surface area of steam activated carbons increased from 185 to 203 m²/g due to an increase in activation time from 15 to 45 min. It also can be seen that micropore volume increased from 0.08 to 0.10 cc/g with an increase in the activation time from 15 to 45 min. Apparently, the increase in the activation time resulted in an increase of the micropore
surface area and volume. At the same time, increases in the median pore diameter with increases in activation time indicated enlargement of the micropores into mesopores. This assumption was confirmed from changes in the micropore size distribution with activation time. It can be seen from the micropore size distribution that the percentage of mesopores (pores larger than 20 Å) increased from 18.9 to 22.0 % with an increase in the activation time from 15 to 45 min. This suggested that an increase in activation time resulted in the reduction of microporosity by widening the micropores. Hence, an activation time of 15 min was used to prepare activated carbon adsorbents.

4.2.4.3. Summary

Though carbon dioxide and steam produced activated carbons of comparable microporosity, the micropore surface areas and volumes of carbon dioxide activated carbons were higher as compared to the ones prepared by steam activation for any level of activation temperature. Furthermore, median pore diameter of carbon dioxide activated carbons were always smaller than those of steam activated carbons indicating the presence of a higher proportion of ultramicroporosity in carbon dioxide activated carbons.

Also, it is seen from the pore size distributions shown in Table 4.5 that the proportions of ultramicroporosity (pores <10 Å) in carbon dioxide activated carbons were slightly higher than steam activated carbons. This was consistent with the higher micropore surface area, micropore volume and median pore diameter of carbon dioxide activated carbons as compared to steam activated carbons. It can also seen from Table 4.5 that though overall microporosity was higher in carbon dioxide activated carbons, steam activated carbons possessed higher proportions of supermicropores (pore size >10 but <20 Å). It can, therefore, be inferred that carbon dioxide activation produced activated carbons with narrower pores as compared to steam activation.
4.2.4.4. Comparison of microporosity of lignite, char and activated carbon

In order to assess the development of microporosity due to carbonization of lignite and subsequent activation of the char, the pore size distribution of the various adsorbents were compared. The pore size distribution of lignite, char (prepared at 475°C for 120 min) and activated carbons (prepared at 650°C for 15 min by steam and carbon dioxide activation) are presented as a bar graph in Figure 4.22.

It can be seen from Figure 4.22 that carbonization of lignite resulted in large increases in the percentage of ultramicropores of size < 5 and <10Å. This is attributed to the opening of numerous pores due to carbonization. It is also interesting to observe that as compared to the activated carbon adsorbents, lignite contained a higher percentage of pores of size <10Å. The proportion of ultramicropores in various lignite-derived adsorbents followed the order: char > lignite > carbon dioxide activated carbon > steam activated carbon.

During activation of char, the pore volume distribution shifted towards larger pore sizes, i.e., supermicropores. The activation process enlarged the ultramicropores to supermicropores and thus increased the proportion of supermicropores (10 < pore size < 20 Å). The proportion of supermicropores followed the order: steam activated carbon > carbon dioxide activated carbon > char > lignite. On the other hand, mesopores changed in the order: lignite > steam activated carbon > carbon dioxide activated carbon > char.

4.2.5 Sulfur dioxide adsorption by activated carbons

Activated carbons obtained from carbon dioxide and steam activation of char were subjected to sulfur dioxide adsorption experiments and the amounts of sulfur dioxide adsorbed by various activated carbons are shown in Figure 4.23.

It can be seen (from Figure 4.23) that in the case of carbon dioxide activation, activated carbon prepared at 650°C exhibited the highest sulfur dioxide adsorption capacity. In contrast, activated carbons made by steam activation showed a
Figure 4.22 Micropore Size Distribution of Lignite, Char (Prepared at 475°C for 120 min) and Activated Carbons (Prepared at 650°C for 15 min by Steam and Carbon Dioxide Activation)
Figure 4.23 Effect of Activation Temperature and Agent on the Sulfur Dioxide Adsorption Capacity of Activated Carbons

[Test conditions: Influent gas composition, 5000 ppm SO2; Bed height, 5.5 cm; Residence time, 4 sec; Adsorption temperature, 125°C; Amount , 1 g]
continuous increase in sulfur dioxide adsorption capacity with activation temperature in the range of 550 to 750°C.

It was observed earlier from the results concerning physical characterization of activated carbons that while in the case of carbon dioxide activation, development in microporosity reached its maximum around $650^\circ$C, in the case of steam activation, microporosity decreased continuously over the range of activation temperatures used in the activation experiments.

In the case of carbon dioxide activated carbon adsorbents, the best adsorbent based on the physical characterization studies also exhibited the highest sulfur dioxide adsorption capacity. This close agreement indicates that the sulfur dioxide adsorption by activated carbon adsorbents are strongly dependent on the fraction of supermicropores. This assumption alone, however, fails to explain the sulfur dioxide adsorption capacity of steam activated carbons. This discrepancy indicates that in addition to sulfur dioxide adsorption in micropores, sulfur dioxide may also be removed by the some other process. In the literature (Davini, 1990), it has been reported that surface oxides of carbon play an important role in the adsorptive removal of sulfur dioxide. Therefore, the discrepancy in the case of sulfur dioxide adsorption by steam activated carbon adsorbents may be attributed to the sulfur dioxide removal by surface oxides. Consequently, it was assumed that even though carbon dioxide and steam activation produced activated carbon of comparable microporosity, steam activation resulted in the production of better activated carbon by incorporating special surface groups in activated carbon adsorbents.

Sulfur dioxide adsorption capacities of activated carbons obtained at $650^\circ$C were compared with that of lignite and char. This is shown in Table 4.4. It can be seen that no significant increase in the sulfur dioxide adsorption capacity was obtained due to carbonization of lignite. However, a large improvement (approximately 150-175 %) in the sulfur dioxide adsorption capacity of lignite was achieved when char was activated using steam and carbon dioxide.

127
4.2.6 Chemical characterization of adsorbents

Physical characterization of lignite, char and activated carbons provided the tool for determining microstructure in terms of their micropore surface area, micropore volume, pore size and pore size distribution. It has already been mentioned that in addition to the microstructure, surface chemical groups also play a major role in the adsorption of SO$_2$ by carbon based adsorbents. In addition, a knowledge about the changes in the surface properties of lignite due to carbonization and activation would also provide useful information concerning the mechanism of carbonization and activation process. Therefore, adsorbents were chemically characterized by FT-IR spectroscopic analysis and an elemental CHN analysis.

4.2.6.1 FT-IR spectroscopic analysis of lignite, char and activated carbons

It has been reported (Davini, 1990) that surface oxides on carbon adsorbents adsorb significant amounts of SO$_2$. As it was observed in this work that steam activated carbons adsorbed higher amounts of SO$_2$ in comparison to carbon dioxide activated carbons, it was decided to carry out Fourier Transformed Infra-red Spectroscopic (FT-IR) studies with the intention of exploring the factors responsible for higher adsorption on steam activated carbons in comparison to the carbon dioxide. FT-IR spectra for different adsorbents are shown in Figure 4.24 to 4.26 for lignite, char and activated carbons, respectively.

A comparison of Figures 4.24 to 4.26 shows that the adsorption centered around 1200 to 1300 cm$^{-1}$ displayed a progressive decrease in intensity during carbonization and activation. In the literature, this band has been assigned to the aromatic C-O vibrations of phenolic groups (Ferraro and Rein, 1985). This observation indicated that the formation of char and activated carbon involved predominantly the loss of alkyl and hydroxyl functional groups.

In the case of activated carbon, changes occurred around 1500 to 1700 cm$^{-1}$ which was the major difference between the char and activated carbons. In literature, the band around 1700 cm$^{-1}$ has been attributed to the aryl alkyl ketone and that of
Figure 4.24 Fourier-Transformed Infrared (FT-IR) Spectrum of Lignite
Figure 4.25 Fourier-Transformed Infrared Spectrum of Char (Prepared at 475°C for 120 min)
Figure 4.2b Comparison of Fourier-Transformed Infrared Spectra of Char (Prepared at 475°C for 120 min) and Activated Carbons (Prepared at 650°C for 15 min by Steam and Carbon Dioxide Activation).

[A: CO₂ Activated carbon; B: Char; C: Steam Activated carbon]
1600 cm\(^{-1}\) for carboxyl group (Ferraro and Rein, 1985). Consequently, the loss of carbonyl and carboxyl group was apparently the general phenomenon due to activation. This result was consistent with the observation concerning the formation of CO\(_2\) and CO due to carbonization of lignite (Section 4.2.3.2). However, high absorption by lignite, char and activated carbon adsorbents in the IR range made the analysis unsuitable for estimating the relative concentration of specific functionalities that can explain higher SO\(_2\) adsorption by steam activated carbons.

4.2.6.2 Elemental analysis of lignite, char and activated carbons

In the literature the C/H ratio has been accepted as an index of condensation reactions or polycyclization reactions common in carbonization and activation. It was, therefore, decided to substantiate the results concerning the microstructure of char and activated carbon by performing an elemental CHN analysis. Elemental analyses of lignite, chars and activated carbons are given in Table 4.6.

It can be seen from Table 4.6 that the H/C ratio has decreased from lignite (0.077) to char (0.037). The decrease in the H/C ratio indicated that carbonization resulted in the increase in the carbon content and decrease in hydrogen content. This is a typical result for any carbonization process as carbonization process is known to improve the aromaticity of parent raw material.

Aromaticity of the char was further increased when char was subjected to activation process. It can be seen from Table 4.6 that in the case of carbon dioxide activated carbon, the H/C ratio decreased progressively from 0.030 to 0.019 to 0.015 due to increases in the activation temperature from 550 to 650 to 750\(^\circ\)C. On the other hand, in the case of steam activated carbon, the H/C ratio decreased progressively from 0.029 to 0.019 to 0.015 due to increase in the activation temperature from 550 to 650 to 750\(^\circ\)C.

In addition to the H/C ratio, O/C and N/C ratios were also calculated and those are presented in Table 4.6. It can be seen from the Table that the O/C ratios of
Table 4.6  Elemental Carbon-Hydrogen-Nitrogen Analysis of Lignite, Char and Activated Carbons

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Carbon (C)</th>
<th>Hydrogen (H)</th>
<th>Nitrogen (N)</th>
<th>Oxygen (O)</th>
<th>H/C</th>
<th>O/C</th>
<th>N/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>55.8</td>
<td>4.30</td>
<td>0.67</td>
<td>39.2</td>
<td>0.077</td>
<td>0.70</td>
<td>0.012</td>
</tr>
<tr>
<td>Char</td>
<td>65.0</td>
<td>2.40</td>
<td>0.88</td>
<td>31.7</td>
<td>0.037</td>
<td>0.49</td>
<td>0.013</td>
</tr>
<tr>
<td>ACC 550</td>
<td>69.7</td>
<td>2.11</td>
<td>0.84</td>
<td>27.3</td>
<td>0.030</td>
<td>0.39</td>
<td>0.012</td>
</tr>
<tr>
<td>ACS 550</td>
<td>68.2</td>
<td>1.97</td>
<td>0.82</td>
<td>29.0</td>
<td>0.029</td>
<td>0.42</td>
<td>0.012</td>
</tr>
<tr>
<td>ACC 650</td>
<td>68.7</td>
<td>1.28</td>
<td>0.87</td>
<td>29.1</td>
<td>0.019</td>
<td>0.42</td>
<td>0.013</td>
</tr>
<tr>
<td>ACS 650</td>
<td>68.5</td>
<td>1.34</td>
<td>0.64</td>
<td>29.5</td>
<td>0.019</td>
<td>0.43</td>
<td>0.010</td>
</tr>
<tr>
<td>ACC 750</td>
<td>68.3</td>
<td>1.01</td>
<td>1.02</td>
<td>29.7</td>
<td>0.015</td>
<td>0.43</td>
<td>0.015</td>
</tr>
<tr>
<td>ACS 750</td>
<td>68.6</td>
<td>1.05</td>
<td>0.64</td>
<td>29.7</td>
<td>0.015</td>
<td>0.43</td>
<td>0.009</td>
</tr>
</tbody>
</table>
lignite, char and activated carbon (carbon dioxide activated) decreased from 0.70 to 0.49 to 0.43. This was consistent with the result that carbonization and activation released oxygenated species such as CO, CO$_2$ and H$_2$O.

It can be seen from the CHN analysis that oxygen-content of lignite was significant. In the literature, development of high microporosity in activated carbons has been attributed to the high oxygen content of the raw material (Mortley et al., 1988). Therefore, it can be mentioned that high O$_2$ content of lignite helped in developing highly microporous activated carbons.

It is seen from the Table that even though the O/C ratios of carbon dioxide and steam activated carbons were not significantly different, the N/C ratios in steam activated carbons were lower as compared to that of CO$_2$ activated carbons and the difference in N/C ratio between steam and CO$_2$ activated carbon adsorbents increased with increase in activation temperature. Therefore it can be assumed that even though the quantities of oxygen containing functionalities present in carbon dioxide and steam activated carbons were similar, steam activation resulted in the formation of higher amounts of nitrogen containing functionalities as compared to CO$_2$ activation.

In the literature, it has been mentioned that activated carbon surface contain both acidic and basic surface oxides (Davini, 1990) which can adsorb SO$_2$. The author reported two different types of carbon oxides present on the surface. These carbon surface oxides may contain O$_2$ and/or N$_2$ as an heteroatom. Consequently, the higher sulfur dioxide adsorption capacity of steam activated carbon was attributed to its higher content of nitrogen containing functionalities as compared to the carbon dioxide activated carbons.
4.3 Phase 3: Effect of additives

In the literature, various transitional metal oxide based catalysts such as CuO/Al$_2$O$_3$ and V$_2$O$_5$, have been used to convert sulfur dioxide into sulfur trioxide. As flue gases contain appreciable quantities of oxygen and water, the probability of the oxidation of sulfur dioxide is very high in the presence of a catalyst. It has already been shown that lignite and lignite-derived activated carbon adsorbents exhibit high adsorption capacity for sulfur dioxide. Generally, any reaction rate is dependent on the extent of adsorption of the participating reactants. So, it can be expected that in the presence of oxygen and water, activated carbon would exhibit significant catalytic activity for the oxidation of sulfur dioxide.

In the case of nitric oxide, various metal-oxide catalysts have been used in order to reduce nitric oxide using a reductant. Activated carbon also has been used as a catalyst for selective catalytic reduction of nitric oxide with ammonia. Therefore, various metal additives such as iron, copper, cobalt and nickel were added to the lignite-based activated carbon adsorbent in order to produce a synergistic effect in its sulfur dioxide and nitric oxide removal performance.

4.3.1 Physical characterization of metal-impregnated activated carbon

From our previous work, sulfur dioxide removal capacities of activated carbon adsorbents were found to be dependent on the supermicroporosity, i.e., pores in the size range of 10-20Å. Removal of SO$_2$ by metal-impregnated activated carbon adsorbents was assumed to be a function of metal type and microporosity. Therefore, a thorough physical characterization of metal-impregnated activated carbon adsorbents was conducted in order to determine their microporosity. Physical characteristics of various metal impregnated activated carbon adsorbents are shown in Table 4.7.

It can be seen from the Table that impregnation of activated carbon with iron did not result in any significant change in micropore volume of activated carbon. A similar trend was observed with micropore surface area and median pore diameter.
<table>
<thead>
<tr>
<th>Physical Characteristics of adsorbents</th>
<th>AC</th>
<th>Fe/AC (Uncalc)</th>
<th>Fe/AC (Calc)</th>
<th>Cu/AC (Uncalc)</th>
<th>Cu/AC (Calc)</th>
<th>Co/AC (Uncalc)</th>
<th>Co/AC (Calc)</th>
<th>Ni/AC (Uncalc)</th>
<th>Ni/AC (Calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum pore volume, cc/g</td>
<td>0.085</td>
<td>0.084</td>
<td>0.065</td>
<td>0.064</td>
<td>0.068</td>
<td>0.054</td>
<td>0.067</td>
<td>0.057</td>
<td>0.072</td>
</tr>
<tr>
<td>(Horvath-Kawazoe method)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Median pore diameter, Å (Horvath-Kawazoe method)</td>
<td>8.3</td>
<td>8.5</td>
<td>12.6</td>
<td>8.8</td>
<td>7.7</td>
<td>8.5</td>
<td>7.6</td>
<td>8.7</td>
<td>8.6</td>
</tr>
<tr>
<td>Micropore surface area, m²/g (Dubinin-Astakhov method)</td>
<td>185.4</td>
<td>170.5</td>
<td>110.4</td>
<td>130.4</td>
<td>145.1</td>
<td>111.6</td>
<td>144.5</td>
<td>117.2</td>
<td>148.6</td>
</tr>
<tr>
<td>Micropore volume, cc/g (Dubinin-Astakhov method)</td>
<td>0.085</td>
<td>0.080</td>
<td>0.065</td>
<td>0.063</td>
<td>0.066</td>
<td>0.053</td>
<td>0.066</td>
<td>0.056</td>
<td>0.071</td>
</tr>
<tr>
<td>Micropore surface area, m²/g (MP method)</td>
<td>100.1</td>
<td>97.2</td>
<td>61.5</td>
<td>72.5</td>
<td>88.2</td>
<td>62.4</td>
<td>87.3</td>
<td>65.3</td>
<td>84.0</td>
</tr>
<tr>
<td>Micropore volume, cc/g (MP method)</td>
<td>0.074</td>
<td>0.078</td>
<td>0.061</td>
<td>0.057</td>
<td>0.066</td>
<td>0.047</td>
<td>0.062</td>
<td>0.050</td>
<td>0.065</td>
</tr>
<tr>
<td>Pore hydraulic radius, Å (MP method)</td>
<td>7.4</td>
<td>8.0</td>
<td>9.9</td>
<td>7.8</td>
<td>7.4</td>
<td>7.5</td>
<td>7.1</td>
<td>7.7</td>
<td>7.8</td>
</tr>
</tbody>
</table>
However, the micropore surface area and volume of the iron-impregnated activated carbon (Fe/AC) adsorbent decreased significantly when it was calcined. The median pore diameter also increased due to calcination indicating that the average pore size of calcined Fe/AC was larger as compared to the uncalcined Fe/AC adsorbent. This can also be seen from Figure 4.27 which shows the changes in the cumulative pore volume of various metal impregnated activated carbon adsorbents before and after calcination. Consequently, the decrease in micropore surface area and volume was attributed to the loss of ultramicroporosity, i.e., loss of the pores in the range of 0-10Å.

On the contrary, impregnation with copper, cobalt and nickel resulted in significant decreases in the micropore volume which was primarily due to the loss of supermicroporosity, i.e., the pores in the size range of 10-20Å. This assumption was made based on the results concerning median pore diameter. Lower median pore diameter of Cu, Co and Ni impregnated activated carbon adsorbents as compared to the unimpregnated activated carbon adsorbent indicated the shift of the pore size distribution towards smaller pore size range. Calcination resulted in an increase in micropore volumes of Cu, Co and Ni/AC adsorbents. This was attributed to the migration of metal oxides into the supermicropores. Therefore, in the case of calcined Cu/AC, Co/AC and Ni/AC adsorbents, the active metal species were located in the supermicropores of activated carbon. In the case of Fe/AC adsorbent, however, active metal species were distributed into the ultramicropores as well as on the outer granule of the activated carbon support.

This conclusion has also been supported by the changes in the differential pore volume distribution of different adsorbents. Two such typical differential pore volume distributions are shown in Figure 4.28 and Figure 4.29 for Fe/AC and Cu/AC, respectively.
Figure 4.27 Comparison of Cumulative Micropore Volume of Calcined and Uncalcined Iron, Copper, Cobalt and Nickel Impregnated Activated Carbons With That of Activated Carbon Alone
Figure 4.28 Comparison of Differential Micropore Volume of Calcined and Uncalcined Iron Impregnated Activated Carbon With That of Activated Carbon Alone
Figure 4.29 Comparison of Differential Micropore Volume of Calcined and Uncalcined Copper Impregnated Activated Carbon With That of Activated Carbon Alone
4.3.2. Temperature programmed reduction of metal-impregnated activated carbons

The main objective of preparing metal-impregnated activated carbon adsorbents was to combine the catalytic activity of the activated carbon support with the strong catalytic activity of the transition metal oxide catalysts. It is known that the rate of any reaction depends on the state of the active material, such as dispersion and valence state. While dispersion or distribution of active material was determined using physical characterization of the metal-impregnated activated carbon adsorbents, the valence state of the active material was assessed using a temperature programmed reduction technique.

Typical temperature programmed reduction spectra of calcined Fe/AC and Cu/AC adsorbents are given in Figures 4.30 and 4.31, respectively.

Figure 4.30 shows that TPR profile of iron on activated carbon exhibited two broad peaks, one at about 405°C and another at about 545°C. The appearance of these two peaks was attributed to two consecutive reduction reactions: \( \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} \) and \( \text{Fe}^{2+} \rightarrow \text{Fe}^{0} \).

On the other hand, Figure 4.31 shows the temperature programmed reduction profile for calcined Cu/AC adsorbent. Calcined Cu/AC adsorbent also exhibited two peaks, one, a very weak peak at the shoulder of second peak, at about 389°C and the other at about 555°C. The presence of these two peaks was attributed to the reduction of \( \text{Cu}^{2+} \) to \( \text{Cu}^{1+} \) and subsequently \( \text{Cu}^{1+} \) to \( \text{Cu}^{0} \).
Figure 4.30 Temperature Programmed Reduction Profile of Iron Impregnated Activated Carbon

[Operating conditions: Heating rate, 4°C/min; Gas composition, 5 % H₂, bal. N₂; Flow rate, 30 mLs/min; Weight of catalyst, 1 g]
Figure 4.31 Temperature Programmed Reduction Profile of Copper Impregnated Activated Carbon

[Operating conditions: Heating rate, 4°C/min; Gas composition, 5 % H₂, bal. N₂; Flow rate, 30 mLs/min; Weight of catalyst, 1 g]
4.4 Phase 4: Adsorptive and reactive removal of sulfur dioxide by metal-impregnated activated carbons

In this phase, sulfur dioxide adsorption characteristics of metal-impregnated activated carbons have been evaluated in the presence and absence of oxygen, and subsequently compared with those of activated carbon. These results will be discussed here.

4.4.1 Sulfur dioxide removal performance of various metal-impregnated activated carbons

Sulfur dioxide adsorption characteristics of metal-impregnated activated carbons were evaluated by generating experimental breakthrough curves. Breakthrough curves show the history of effluent sulfur dioxide concentration with time. These curves were analyzed in order to determine breakthrough times, which corresponded to the time-on-run for effluent sulfur dioxide concentration to reach 100 ppm. In addition, yield of sulfur dioxide removal was also determined from the breakthrough curves. In an adsorption process, where the adsorbate is not only removed by adsorption but also by reaction, it is very difficult to differentiate between the adsorptive and reactive removal. In this study, while breakthrough time has been considered to evaluate removal of sulfur dioxide by adsorption, yield of sulfur dioxide has been used to determine the removal of sulfur dioxide by reaction. Yield of sulfur dioxide removal was estimated from the difference between influent and effluent sulfur dioxide concentration after the breakthrough time of the breakthrough curve. Details are presented here.

Adsorption experiments, carried out to test sulfur dioxide adsorption characteristics of lignite-derived activated carbon and metal-impregnated activated carbons, in the absence of oxygen, used the following operating conditions: adsorption temperature, 125°C; adsorber bed height, 5.5 cm; adsorbent particle
diameter, 4 mm; influent flow rate, 100 mLs/min; residence time, 4 sec; influent gas composition, 5000 ppm of SO₂, bal. N₂.

In an ideal plug flow system with no resistance to mass transfer, the effluent concentration response would replicate the influent concentration with a time delay corresponding to the hold-up in the column. In a real system, the effluent concentration response is always dispersed as a result of combined effects of axial dispersion and mass transfer resistances. Measurement of the time delay therefore provides information concerning the adsorption equilibrium while measurement of the dispersion of the response provides information on the adsorption kinetics and the extent of the axial mixing in the column. As it was inferred from the results obtained from the sulfur dioxide adsorption on lignite that there was little or no axial dispersion in the column under the operating conditions used, the shape of the breakthrough curves was taken as an indication of the sorption kinetics.

Figure 4.32 shows breakthrough profiles of sulfur dioxide on activated carbon and various metal-impregnated activated carbons in the absence of oxygen. It can be seen from Figure 4.32 that there were no significant differences in the shape of the sulfur dioxide breakthrough profiles over activated carbon and metal-impregnated activated carbons indicating that the rate controlling mechanism for sulfur dioxide removal over various adsorbents was similar under the operating conditions used. It also can be seen from the Figure that impregnation of activated carbon with Cu, Co and Ni resulted in a reduction in the sulfur dioxide adsorption capacity of activated carbon. However, a significant improvement in the sulfur dioxide adsorption capacity was achieved when activated carbon was impregnated with Fe.

The breakthrough times of sulfur dioxide, with and without oxygen, through the beds of metal-impregnated activated carbons as well as unimpregnated activated carbon are shown in Table 4.8. It can be seen from the Table that, in the absence of oxygen, the sulfur dioxide breakthrough time and consequently, sulfur dioxide
Figure 4.32 Sulfur Dioxide Breakthrough Profiles on Activated carbon and Metal Impregnated Activated Carbons in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 5000 ppm SO₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Table 4.8 Sulfur Dioxide Breakthrough Time on Various Metal-Impregnated Activated Carbon Adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Breakthrough time min</th>
<th>Adsorption capacity g of SO$_2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without O$_2$</td>
<td>With O$_2$</td>
</tr>
<tr>
<td>Lignite</td>
<td>15.3</td>
<td>26.1</td>
</tr>
<tr>
<td>Ac</td>
<td>30.3</td>
<td>36.5</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>36.6</td>
<td>37.2</td>
</tr>
<tr>
<td>Cu/AC</td>
<td>20.0</td>
<td>54.9</td>
</tr>
<tr>
<td>Cu/AC$^R$</td>
<td>20.0</td>
<td>73.6</td>
</tr>
</tbody>
</table>
adsorption capacity of various adsorbents, in decreasing order of performance, were as follows: Fe/AC > AC > Cu/AC = Co/AC = Ni/AC.

Sulfur dioxide adsorption capacity was assumed to be a function of microporosity as well as the nature of the metal. It was observed from the physical characterization of metal-impregnated activated carbons that impregnation with copper, cobalt and nickel nitrate resulted in partial introduction of CuO, Co$_2$O$_3$ and NiO into the porous system of activated carbon adsorbent resulting in the reduction in the proportion of supermicroporosity (pores in the size ranging from 10 to 20Å$^\circ$). Iron, on the other hand, distributed mostly on the outer surface of the activated carbon grains as can be seen from the insignificant loss of micropore surface area and volume. During calcination, iron oxide partially redistributed over the activated carbon granule with consequent loss in the microporosity. However, that loss in microporosity was attributed to the loss of ultramicroporosity, i.e., the pores in the range of 0 to 10 Å$^\circ$. Previously, it was observed that the sulfur dioxide adsorption capacity of activated carbon adsorbents were strongly dependent on the fraction of supermicropores. Therefore, the increase in sulfur dioxide adsorption capacity of activated carbon due to impregnation with iron additive was consistent because, in the case of Fe/AC adsorbent, supermicroporosity did not change very significantly as compared to activated carbon adsorbent. In addition, deposition of the iron on the surface of activated carbon granule added to the adsorption capacity of Fe/AC adsorbent.

Interestingly, except for activated carbon, effluent sulfur dioxide concentrations for other metal-impregnated activated carbons (Iron, Copper, Cobalt impregnated activated carbons) did not reach the influent sulfur dioxide concentration. Sulfur dioxide concentrations in the outlet are either constant at a value lower than the influent sulfur dioxide concentration or increased slowly until the influent concentration was reached. This phenomenon indicated the possibility of the existence of another process which, at this point, was assumed to be surface chemical reaction.
4.4.2 Effect of oxygen and the valence state of the active metal species on the adsorption characteristics

It was assumed in the previous section that in addition to physical adsorption, sulfur dioxide was also removed by surface chemical reaction. To find out the effect of the oxidation state of the metal on the removal of SO$_2$, copper supported on activated carbon was reduced at 450°C under the flow of hydrogen in situ before the adsorbent was subjected to the sulfur dioxide adsorption experiment. Sulfur dioxide breakthrough curves for reduced and unreduced copper-carbon adsorbents in the absence of oxygen are shown in Figure 4.33. It can be seen that the oxidation state of the metal did not show any effect on the sulfur dioxide adsorption capacity.

However, in the presence of oxygen, the response was very different as can be seen. Figure 4.34 shows the breakthrough profiles of sulfur dioxide over reduced and unreduced copper impregnated activated carbon adsorbents in the presence of oxygen. There was a large improvement in the sulfur dioxide removal performances which can be attributed to the combined effect of oxygen as well as to in-situ reduction of the copper impregnated activated carbon adsorbent by hydrogen. However, it is very difficult to differentiate the individual effect of oxygen and valence state of the metal at this point. Therefore, subsequent sulfur dioxide removal experiments in the presence of oxygen were carried out with reduced adsorbents.

4.4.3. Effect of oxygen on the sulfur dioxide removal performance

As flue gases contain appreciable amounts of oxygen, the influence of oxygen on the adsorption of sulfur dioxide by lignite, activated carbon and various metal impregnated activated carbons have been studied by using a gas mixture containing 3000 ppm SO$_2$, 6.5 % O$_2$ and balance N$_2$ under the same operating conditions as mentioned in the previous section.

Figure 4.35 shows the typical sulfur dioxide breakthrough profiles over lignite in the presence and absence of oxygen. It can be seen from the Figure that
Figure 4.33 Sulfur Dioxide Breakthrough Profiles on Reduced and Unreduced Copper Impregnated Activated Carbons in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 5000 ppm SO$_2$; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Figure 4.34 Sulfur Dioxide Breakthrough Profiles on Reduced and Unreduced Copper Impregnated Activated Carbons in the Presence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 3000 ppm SO$_2$ and 6.5 % O$_2$; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Figure 4.35 Typical Sulfur Dioxide Breakthrough Profiles on Lignite in the Presence and Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 3000-5000 ppm SO₂ and 0-6.5 % O₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
there are two distinct differences in the nature of sulfur dioxide breakthrough profiles in the presence and absence of oxygen.

In the absence of oxygen, once sulfur dioxide broke through the lignite bed, effluent sulfur dioxide concentrations reached the influent sulfur dioxide concentration rapidly. On the other hand, in the presence of oxygen, the effluent sulfur dioxide concentration oscillated around a value of 65 % of the influent sulfur dioxide concentration for about 60 min before increasing to the influent sulfur dioxide concentration level.

It was observed that in the absence of oxygen, the yields of sulfur dioxide on metal-impregnated activated carbon adsorbents were very low. However, in the presence of oxygen, the yields of sulfur dioxide over lignite and activated carbon were very significant. These phenomena supported the assumption that sulfur dioxide was removed by surface chemical reactions.

The breakthrough profiles of sulfur dioxide in the presence of oxygen over lignite, activated carbon, Fe/AC and Cu/AC are shown in Figure 4.36. Sulfur dioxide breakthrough times as well as adsorption capacities are also shown in Table 4.8. It can be seen from the Table that in the presence of oxygen, sulfur dioxide breakthrough times and adsorption capacities, in decreasing order of performance, are as follows: Cu/AC >> Fe/AC > AC = Lignite.

It can also be seen from the Table that in the presence of oxygen, no significant improvement in the sulfur dioxide removal performance of activated carbon has been achieved due to its impregnation with iron additive. As observed earlier in the absence of oxygen, there was a significant difference in the breakthrough time of sulfur dioxide over Fe/AC as compared to that on unimpregnated activated carbon. It can be seen here that even though the sulfur dioxide removal performance of activated carbon improved due to the presence of oxygen, that of Fe/AC did not show any significant improvement. It has been discussed earlier that impregnation of activated carbon with the iron additive resulted in the deposition of the active metal species on the active carbon granule.
Figure 4.36 Sulfur Dioxide Breakthrough Profiles on Reduced Copper and Iron Impregnated Activated Carbons, As Well As Activated Carbon Alone, in the Presence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 3000-5000 ppm SO₂ and 0-6.5 % O₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
which, during calcination, partially migrated into the ultramicropore structure. As ultramicropores imposed higher diffusional resistances for the reactants, those metals were not used and consequently, sulfur dioxide removal performances of Fe/AC did not improve significantly. Even though active iron metal species deposited partially on the outer surface helped in the removal of sulfur dioxide, the effect could not compensate the loss of sulfur dioxide adsorption capacity due to the loss in activated carbon surface.

It can also be seen from Figure 4.36 as well as from Table 4.8 that a tremendous improvement in the sulfur dioxide removal performance was achieved with Cu/AC. Sulfur dioxide breakthrough times on reduced, unreduced Cu/AC and activated carbon alone were 73.6, 54.9 and 20.0 min, respectively. In addition to the tremendous improvement in the breakthrough time, a very significant improvement in the yield of sulfur dioxide was also achieved. This tremendous improvement in the sulfur dioxide removal performance in the presence of oxygen with Cu/AC adsorbent was attributed to the catalytic activity of the active Cu-species for the reactive removal of sulfur dioxide. Furthermore, it also can be seen that copper at its lower valence state was more active for the reactive removal of sulfur dioxide (Table 4.8).

4.4.4 Reaction mechanism for the removal of sulfur dioxide

It was observed during the sulfur dioxide adsorption experiments in the presence of oxygen that effluent sulfur dioxide concentrations oscillated. This observation was reproducible in all the sulfur dioxide adsorption experiments in the presence of oxygen. Oscillation in the sulfur dioxide breakthrough curves on activated carbon and particularly metal impregnated activated carbon adsorbents was never reported in the literature before. However, oscillation in the reaction rate and, hence yield has been reported very recently in the case of reaction between nitric oxide and carbon monoxide. In the literature (Matros, 1990), various reasons have been given in order to explain oscillation in the yield or reaction rate. These are (Renken, 1990):
(1) surface coverage dependent reaction rate and preexponential factor,
(2) surface inhomogeneity of the adsorbent,
(3) competition between reactions with varying relaxation times and
(4) presence of different types of active centers.

In real situations, every reaction rate equation should contain coverage dependent rate and exponential terms. Also, in most cases, the adsorbents or catalysts contain surface inhomogeneities. From the above-mentioned factors responsible for oscillation in reaction rate, one can expect that every reaction system should exhibit oscillations. However, in real situations, global oscillations do not take place due to lack of synergism. In the case of sulfur dioxide adsorption on lignite-derived adsorbents, in the presence of oxygen, the oscillation in the breakthrough profiles can thus be attributed primarily to the presence of different types of active centers. Activated carbon, prepared from lignite, contains significant amounts of inorganic materials, most of which are known to possess catalytic activity for the oxidation of sulfur dioxide into sulfur trioxide. The situation becomes worse when further metal additives are impregnated into the activated carbon adsorbent. This observation, i.e., large oscillations in the sulfur dioxide breakthrough profiles due to incorporation of additional metal oxides, substantiated the assumption that the presence of different active sites was one of the contributing factors for producing oscillations in the breakthrough curves. In addition, competition between different reactions with different rates can also be responsible for the oscillations which will be explained in the following paragraph.

In the literature, it has been stated that one of the characteristics of the activated carbon adsorbents is the presence of acidic as well as basic surface oxides (Richter, 1990; Davini, 1992). These surface oxides also can be formed during the course of adsorption and reaction when oxygenated species are adsorbed on the surface. In the absence of oxygen, the formation of surface oxides was due to adsorption of sulfur dioxide on the activated carbon support.
A plausible mechanism or reaction scheme which considers all these observations from the experiments is given below:

1. In the case of activated carbon adsorbents, sulfur dioxide is adsorbed on an oxygen atom of a carbon surface oxide as a $<\text{SO}_2\text{-O}>$ complex.

2. $\text{O}_2$ is adsorbed on activated carbon support producing more surface oxides.

3. In the case of metal-impregnated activated carbon adsorbents or catalysts, in addition to step 1, sulfur dioxide as well as oxygen also can be adsorbed on the active metal species. Sulfur dioxide and oxygen, adsorbed on the neighbouring sites, may react to produce an $<\text{SO}_2\text{-O}>$ complex.

The influence of oxygen on the reaction velocities can thus be interpreted by this reaction scheme. In the absence of oxygen, the formation of surface oxides was negligible which explained the zero yield of sulfur dioxide on lignite and other lignite-derived adsorbents. Physical adsorption of sulfur dioxide was the predominant phenomenon on lignite, char and activated carbon adsorbents in the absence of oxygen. This was due to the fact that negligible amounts of sulfur dioxide were adsorbed chemically on the lignite, char and activated carbon surfaces. In the case of metal-impregnated activated carbon adsorbents, metal species chemically adsorbed sulfur dioxide and oxygen, which was consistent with the very low yield of sulfur dioxide on the metal-impregnated activated carbons in the absence of oxygen.

In the presence of oxygen, reformation of the surface oxides was much faster as compared to that in the case where there was no oxygen. As a consequence, yields of sulfur dioxide removal increased in the presence of oxygen. This increase in the reaction yield of sulfur dioxide was consistent with the assumption that in the presence of oxygen, in addition to physical adsorption, sulfur dioxide also was removed by a surface chemical reaction.
4.5 Phase 5: Adsorptive and reactive removal of nitric oxide by lignite and various lignite-derived adsorbents

In the literature (Richter et. al., 1990), activated carbon has been reported to have been used as the low temperature catalyst for selective catalytic reduction of NO. As the activated carbon based process works at lower operating temperatures than the conventional SCR system ($V_2O_5$), adsorption of various reacting gases plays an important role in the overall reaction kinetics. Though considerable research work has been carried out on the selective catalytic reduction (SCR) of NO on various activated carbons, very little information is available in the literature on the adsorption characteristics of NO on lignite, lignite-derived char, activated carbon and metal-impregnated activated carbon.

In this phase of work, the NO adsorption characteristics of Saskatchewan lignite, and various other lignite-derived adsorbents such as char, activated carbon and metal-oxide impregnated activated carbons have been studied in order to provide an understanding of the NO removal processes over carbon-based adsorbents. In addition, the effects of both the presence of oxygen and the valence state of the active metal species on the NO adsorption by metal-impregnated activated carbon adsorbents were also studied.

The NO removal studies were carried out over lignite, char, activated carbon, and reduced and unreduced Fe, Cu, Co and Ni impregnated activated carbons in a 12.7 mm (1/2 in.) diameter microreactor in the presence and absence of oxygen. The operating variables were: temperature, 125°C; influent NO and $O_2$ concentration; 400-1100 ppm and 0-6.5 %, respectively; particle size, 4 mm; residence time, 4 sec.

NO adsorption characteristics of lignite and other lignite-derived adsorbents were evaluated by generating experimental breakthrough curves. In this work, three different terms have been used to take care of the adsorptive and reactive removal of NO by various adsorbents and those are NO adsorption capacity, overall NO removal efficiency and yield of NO. NO adsorption capacity of the adsorbent was evaluated
from the amount of NO adsorbed up to the breakthrough point which corresponded to 50 ppm NO in the effluent stream. The yield of NO, which was indicative of the removal of NO by reaction after the breakthrough point, was estimated from the difference between the influent and effluent adsorbate concentrations. The overall NO removal efficiency was calculated from the information concerning the total amount of NO that went in \( (\text{NO}_{\text{in}}) \) and total amount of NO that came out \( (\text{NO}_{\text{out}}) \) of the adsorber during the entire experiment.

4.5.1 NO oxide adsorption on lignite, char and activated carbon

Figure 4.37 shows the NO breakthrough profiles on lignite, char and activated carbon. While Table 4.9 gives the comparison of the overall NO removal efficiencies of various adsorbents in the presence and absence of oxygen, Table 4.10 contains information on NO breakthrough times of various adsorbents.

In the absence of oxygen, NO removal experiments were carried out with 1100 ppm of NO. However, in the presence of oxygen, influent NO concentration was 400 ppm. An NO adsorption experiment on activated carbon was also carried out using 400 ppm NO as the influent concentration in the absence of oxygen with activated carbon (AC).

It can be seen from Figure 4.37 that although the NO breakthrough times for activated carbon and char were not significantly different as compared to lignite, there was a significant difference in the yield of NO on activated carbon as compared to char and lignite. Figure 4.37 also shows that in the case of lignite, char and activated carbon, once NO broke through the bed, effluent NO concentration steadily reached the influent NO concentration. However, in the case of lignite, char and activated carbon, the effluent NO concentration was always less than the influent NO concentration which was considered as the unsteady state yield over the time period studied. It can be seen from Figure 4.37 that the yield of NO followed the order: lignite \( \approx \) char \( < \) activated carbon. This increase in yield of NO was also reflected in the overall NO removal performance which is shown in Table 4.9. It
Figure 4.37 Nitric Oxide Breakthrough Profiles on Lignite, Char and Steam Activated Carbons in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 1103 ppm NO bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Table 4.9 Overall Nitric Oxide Removal Efficiencies of Various Lignite-Derived Adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>In the absence of oxygen*</th>
<th>In the presence of oxygen**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NO_{ads}, g</td>
<td>NO_{in}, g</td>
</tr>
<tr>
<td>Lignite</td>
<td>1.1</td>
<td>14.0</td>
</tr>
<tr>
<td>Char</td>
<td>2.4</td>
<td>14.0</td>
</tr>
<tr>
<td>AC</td>
<td>3.4</td>
<td>15.0</td>
</tr>
<tr>
<td>AC++</td>
<td>0.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>2.7</td>
<td>11.0</td>
</tr>
<tr>
<td>Fe/AC (R)</td>
<td>14.2</td>
<td>24.0</td>
</tr>
<tr>
<td>Cu/AC (R)</td>
<td>10.7</td>
<td>24.0</td>
</tr>
<tr>
<td>Co/AC (R)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Ni/AC (R)</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

* Experiments were not performed
(R) Catalysts were reduced by hydrogen
+ NO influent concentration of 1100 ppm
++ NO influent concentration of 400 ppm.
Table 4.10 Nitric Oxide Breakthrough Time on Various Lignite-Derived Adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Breakthrough Time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without O2</td>
</tr>
<tr>
<td>Lignite</td>
<td>5.1</td>
</tr>
<tr>
<td>Char</td>
<td>5.1</td>
</tr>
<tr>
<td>AC (1)</td>
<td>5.3</td>
</tr>
<tr>
<td>AC (2)</td>
<td>7.1</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>5.1</td>
</tr>
<tr>
<td>Fe/AC</td>
<td>30.4</td>
</tr>
<tr>
<td>Cu/AC</td>
<td>10.5</td>
</tr>
<tr>
<td>Ni/AC</td>
<td>*</td>
</tr>
</tbody>
</table>

AC (1) : Influent NO concentration was 1100 ppm

AC (2) : Influent NO concentration was 400 ppm

*: Experiments were not performed
can be seen that a very significant improvement in the overall NO removal efficiency was achieved due to carbonization and activation of lignite. The overall NO removal efficiency of activated carbon (22.7%) was significantly higher as compared to char and lignite (17.1 and 7.9%, respectively). At this point, it is relevant to mention that lignite, char and particularly activated carbon exhibited high sulfur dioxide adsorption capacity which was correlated with their microporosity. Details concerning those results have already been discussed in phase 2. However, in the case of nitric oxide removal, in spite of the large differences in the microporosity between lignite, char and activated carbon, NO breakthrough times were the same for all those adsorbents. In addition, NO breakthrough times were significantly shorter as compared to sulfur dioxide breakthrough times over all the unimpregnated carbon based adsorbents even though molecular dimensions of sulfur dioxide and nitric oxide are not very different. So, it was assumed that while removal of sulfur dioxide by carbon based adsorbents was diffusion controlled, removal of nitric oxide was primarily kinetically controlled. Consequently, removal of NO on char and activated carbon was attributed to the surface chemical reaction of NO with the carbon surface.

4.5.2 NO oxide adsorption on metal-impregnated activated carbons

In order to examine the effect of metal impregnation on NO removal performance of activated carbon, adsorption experiments were also carried out with metal-impregnated activated carbons.

Table 4.10 shows that impregnation of activated carbon with iron additives did not improve the breakthrough times and consequently, NO adsorption capacity. In fact, breakthrough time for NO on Fe/AC was shorter (5.1 min) than that on activated carbon alone (5.3 min). On the other hand, Table 4.9 shows that the overall NO removal efficiency of Fe/AC (24.5%) was higher when compared to activated carbon alone (22.7%). This phenomenon could be explained with the help of the results obtained from physical characterization of the adsorbents which has been shown in Table 4.7. It can be seen from the Table that micropore volume and surface
area did not change significantly due to impregnation of activated carbon with iron additives alone. So, impregnation of the activated carbon with ferric nitrate resulted in the distribution of active species mostly on the outer surface of the activated carbon granule. This deposition resulted in the loss of activated carbon surface and introduced metal nitrates on the surface. However, calcination of Fe/AC adsorbent resulted in a significant decrease in the micropore volume and surface area indicating the partial migration of iron oxide into the porous system. The increase in the overall NO removal efficiency due to the addition of iron could not compensate for the decrease in adsorption due to loss in microporosity and surface of the activated carbon resulting in a net decrease in the overall NO removal efficiency. A similar observation was made by Grzybek et. al. (Grzybek, 1992).

Nitric oxide adsorption experiments were also carried out with lower influent nitric oxide concentrations. Table 4.10 shows the typical results obtained from those experiments. It is seen from Table 4.10 that low influent NO concentration (400 ppm) resulted in longer NO breakthrough time as compared to those obtained with higher influent NO influent concentration (1100 ppm) and consequently, a better adsorption performance was achieved with lower NO concentration. This phenomenon can be explained as follows: adsorption isotherm relates equilibrium amount of adsorbate adsorbed with concentration of the adsorbate as \( q = f(C) \). For a linear adsorption \( q = K \cdot C \) isotherm, the change in the \( q / C \) (where 'q' is the equilibrium amount of NO adsorbed and 'C' is the influent NO concentration) is a constant, so that the breakthrough time should not be affected by different influent NO concentrations. However, in this case the adsorption of NO on carbon based adsorbents followed a non-linear favorable isotherm like \( q = \frac{aC}{(1+bC)} \), which resulted in an increase in the breakthrough time due to the decrease in the influent NO concentration.
4.5.3 Effect of valence state on the nitric oxide removal performance of the metal-impregnated activated carbon adsorbents

In the literature (Shelef and Kumar, 1971), it has been mentioned that chemisorption of NO on transition metal oxides is affected by the valence state of the metal species. For example, the chemisorption capacity of copper oxides follows the order: $\text{Cu}^0 > \text{Cu}^{+1} > \text{Cu}^{+2}$. Although, this information was available from the literature, it was never exploited to improve adsorption capacity of metal-impregnated activated carbons. So, it was decided to examine the effect of reduction of metal species on the NO breakthrough characteristics on various metal impregnated activated carbon adsorbents.

It can be seen from figure 4.38, which compares NO breakthrough curve on activated carbon with that on Fe/AC, that impregnation with iron additives did not improve the NO removal performance of activated carbon. However, it can be seen from Figures 4.39 and 4.40, which show the NO breakthrough profiles on activated carbon and reduced Fe/AC adsorbent, and reduced and unreduced iron-impregnated activated carbon, that a tremendous improvement in the NO removal performance was achieved when Fe/AC adsorbent was reduced in-situ by flowing hydrogen. It can also be seen from Figures 4.39 and 4.40 that a very significant improvement in NO removal performance was achieved both in terms of breakthrough time as well as NO yield.

Table 4.10 shows that NO breakthrough time on reduced Fe/AC adsorbent about 400% higher than that on the unreduced Fe/AC. Also, it can be seen from Table 4.9 that reduced Cu/AC adsorbent exhibited significant improvement in the NO removal performance over activated carbon alone. The overall NO removal efficiency for activated carbon and reduced Cu/AC were 25.9 and 44.6%, respectively. Therefore, it was concluded that the adsorption of NO on these metal-impregnated activated carbon adsorbents with the metal in the higher oxidation state is low compared to those in the lower oxidation states. As, in general, rate of reaction velocity is proportional to the extent of adsorption, it can be said that reduced Fe/AC
Figure 4.38 Nitric Oxide Breakthrough Profiles on Steam Activated Carbon and Unreduced Iron Impregnated Activated Carbon in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 1103 ppm NO bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Figure 4.39 Nitric Oxide Breakthrough Profiles on Activated carbon and Reduced Iron Impregnated Activated Carbon in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 1103 ppm NO bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Figure 4.40 Nitric Oxide Breakthrough Profiles on Activated Carbon, and Reduced and Unreduced Iron Impregnated Activated Carbons in the Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 1103 ppm NO bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
and Cu/AC adsorbents would be more active in the reactions of NO as compared to the unreduced Fe/AC and Cu/AC adsorbents.

4.5.4 Effect of oxygen on nitric oxide removal performance

It has been observed from our work that a tremendous improvement in the overall NO removal efficiency can be achieved when iron and copper-impregnated activated carbon adsorbents are reduced by hydrogen. In any reaction involving the reduction of NO by a reducing agent, it is important to know whether the use of the reducing agent is selective for nitric oxide as opposed to the reaction in which oxygen competes with NO for the same reducing agent. Therefore, it was interesting to examine the effect of oxygen on the NO removal over various carbon-based adsorbents.

Adsorption experiments were carried out in the presence of oxygen to test NO adsorption characteristics of lignite and various other lignite-derived adsorbents. The following operating conditions were used: adsorption temperature, 125°C; residence time, 4 sec; influent NO concentration, 400 ppm; influent oxygen concentration, 6.5%; and particle size, 4 mm.

As it was observed earlier that reduced metal-impregnated activated carbon adsorbents performed better than the unreduced ones, NO adsorption experiments, in the presence of oxygen, were carried out with reduced adsorbents.

Effect of oxygen on NO removal efficiency of activated carbon

It can be seen from Table 4.10 that in the presence of oxygen, breakthrough times for NO increased from 7.13 min (in the absence of oxygen) to 11.45 min (in the presence of oxygen). This phenomenon indicated that the presence of oxygen improved the NO breakthrough time. Also it can be seen from Table 4.9 that in the presence oxygen, the overall NO removal efficiency of activated carbon increased from 25.9 to 36.2%. This improvement in the overall NO removal efficiency may thus be attributed to the improvement in the NO removal due to an increase in the
reaction yield. Consequently, it can be assumed that in the presence of oxygen, the removal of NO was not only by adsorption but also by surface chemical reaction and, the presence of oxygen, in general, increased the reaction rate for the removal of NO. This was also supported by the higher yield of nitric oxide removal in the presence of oxygen. A similar observation was made by Richter et. al. (Richter, 1990).

**Metal-impregnated activated carbons**

It has already been mentioned that in the absence of oxygen, reduced Fe/AC exhibited tremendous improvement in the NO removal performance and the presence of oxygen, in general, increased overall NO removal performance of all the adsorbents. However, it was interesting to note (Table 4.9) that in the presence of oxygen, NO removal efficiency of reduced Fe/AC decreased significantly as compared to its overall NO removal efficiency in the absence of oxygen. It can be seen from Table 4.9 that the overall NO removal efficiency decreased from 59.5 to 44.4% while the NO breakthrough time decreased from 30.4 to 16.8 min in the presence of oxygen (Table 4.10). This decrease in the NO removal performance of reduced Fe/AC in the presence of oxygen was attributed to the reoxidation of iron by adsorbed NO or oxygen. A similar observation was made by Poling and Eischens (Poling and Eischens, 1966). However, the overall NO removal efficiency of the reduced Fe/AC in the presence of oxygen (44.4%) was still higher than the efficiency of the unreduced Fe/AC adsorbent (24.5%) and AC (25.9%) in the absence of oxygen. This was an interesting observation as the oxidation of reduced Fe species was partial even in the presence of 6.5% O₂.

Figure 4.41 shows the NO breakthrough profile of various metal-impregnated activated carbon adsorbents in the presence of oxygen. It can be seen that NO breakthrough time on Ni/AC adsorbent was longer than that on Fe, Cu and Co/AC adsorbents. In the presence of oxygen, metal-impregnated activated carbon adsorbents showed NO yields in the following order: Fe/AC ≈ Cu/AC > Ni/AC >
Figure 4.41 Nitric Oxide Breakthrough Profiles on Reduced Iron, Copper, Cobalt and Nickel Impregnated Activated Carbons in the Presence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 400 ppm NO, 6.5 % O₂, bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Co/AC. Although the overall NO removal efficiencies followed the order: Ni/AC > Cu/AC > Co/AC > Fe/AC, the differences in their performances were not very pronounced. This behavior can be explained on the basis of the physical characteristics of the adsorbents shown in Table 4.9. It can be seen from this table that micropore surface areas of the calcined metal-impregnated activated carbon adsorbents decreased in an order which was similar to the order of their overall NO removal efficiency. However, in the case of calcined Fe/AC adsorbent, the micropore surface area was significantly lower compared to the other impregnated adsorbents. Even though the literature (Ahmed et. al., 1992) indicates no correlation between the surface area (BET) with the adsorbents NO adsorption capacity, our results show that the NO removal efficiency could be correlated with micropore surface area. The NO removal efficiency of the adsorbents was observed to increase with the micropore surface area.
4.6 Simultaneous removal of SO₂ and NO

In the previous Sections single component adsorption performances of various adsorbents were evaluated in terms of their SO₂ or NO adsorption capacities in the presence and absence of O₂. However, actual power plant flue gases contain SO₂, NO, O₂ and H₂O. As the presence of one component can significantly change the adsorption of other components on activated carbon adsorbents, it was necessary to carry out experiments in order to find out the effect of SO₂ on the adsorption of NO and vice versa in the presence of oxygen.

In addition, in the literature (Armor, 1990) selective catalytic reduction (SCR) of NO using NH₃ over a catalyst has been described as the best available commercial technology for the removal of NO. From our studies on the SO₂ and NO adsorption by lignite and other lignite-derived adsorbents, it has been observed that lignite-derived activated carbons and metal-impregnated activated carbons exhibited high NO removal performances both in terms of adsorption and surface chemical reaction. As, in most of the cases, rate of reaction is proportional to the extent of adsorption of various reacting components on the catalyst, lignite-derived activated carbon adsorbents, particularly metal-impregnated activated carbons may be considered as a potential SCR catalyst. However, it has been reported (Bosch and Jannsen, 1988) that SO₂ acts as a poison for most of the SCR catalysts such as V₂O₅/TiO₂. Therefore, it was interesting to examine the NO removal performance of our activated carbon and metal-impregnated activated carbons in the presence of SO₂.

Tests performed to study the simultaneous removal of SO₂ and NO in the presence of O₂ used the following operating conditions: adsorbent particle size, 3.6 mm; adsorption temperature, 125°C; residence time, 4 sec and influent gas composition, 3000 ppm SO₂, 400 ppm NO, 5.0 vol% O₂ in N₂.

Figure 4.42 shows the breakthrough profiles of SO₂ and NO in the presence of O₂ on lignite. It can be seen from the Figure 4.42 that in the presence of SO₂, NO breakthrough time over lignite did not change significantly. However, a significant
Figure 4.42 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Lignite in the Presence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition. 400 ppm NO, 3000 ppm SO₂, 5% O₂, bal N₂; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
decrease in the SO$_2$ breakthrough time on lignite was noticed due to the presence of NO (12.5 min as compared to 26.1 min of SO$_2$ breakthrough time on lignite in the presence of O$_2$).

It was interesting that SO$_2$ concentration was raised to a concentration above the influent SO$_2$ concentration (C/C$_0$ > 1). This was explained as follows: as the NO adsorption proceeded down the lignite bed, competitive binary adsorption regime was set in, resulting in the displacement of some previously adsorbed SO$_2$. It was observed from previous adsorption experiments with SO$_2$ and NO that while adsorption of SO$_2$ was controlled by the diffusion of SO$_2$ into the micropores, that of NO was kinetically controlled and was dependent on the surface. In addition, it is known from the literature (Davini, 1990) that activated carbon surface contains surface oxides which can adsorb SO$_2$ and NO. Therefore, stronger adsorption of NO on the surface oxides in comparison to that of SO$_2$ caused a consequent decrease in the SO$_2$ adsorption capacity in the presence of O$_2$.

This phenomenon may have significance in practical applications, since for example the SO$_2$ could be enriched inside the column when used in stack gas clean up. Of course, to take advantage of this phenomenon, the adsorption step must be stopped prior to breakthrough, and desorption should be carried out concurrently with the adsorption. Also, to take advantage of economic potentials, the reactivation step may have to be split into steps to separate a SO$_2$ rich desorbate.

Figure 4.42 also shows that a high yield of NO was achieved up to approximately 150 min of time-on-run. This phenomenon may be explained as follows: SO$_2$, in the presence of O$_2$, reacts with the metal oxides (present in the lignite) to form respective sulfates. It has been reported that metal sulfates show better NO adsorption capacities as compared to respective oxides. For example in a CuO/Al$_2$O$_3$ process for simultaneous removal of SO$_2$ and NO from power plant flue gases, it has been observed that CuO reacts with SO$_2$ and O$_2$ (present in the flue gas) to form CuSO$_4$ which acts as a SCR catalyst for the removal of NO by NH$_3$. Therefore, it can be assumed that metals in lignite participate in the same way as CuO.
in CuO/Al₂O₃ for the removal of NO. However, as the percentage of metals in lignite is small, the effect was not very pronounced.

The percentage of already present metals increased during carbonization and activation of lignite. When some additional metal oxides were incorporated into the activated carbon support during the preparation of metal-impregnated activated carbon catalysts, a tremendous improvement in the NO adsorption capacity was observed. While Figure 4.43 shows the simultaneous removal of SO₂ and NO in the presence of O₂ over reduced iron impregnated activated carbon (Cu/AC) adsorbent, Figure 4.44 shows the same on Cu/AC adsorbent.

It can be seen that in the case of Fe/AC (Fig. 4.43), in the presence of oxygen, NO was completely removed from the mixture since ca. 60 min till the end of the run (150 min). On the other hand, SO₂ removal performance of Fe/AC adsorbent in the presence of oxygen was significantly lower as compared to the case where NO was not present (37.2 min of SO₂ breakthrough time).

Figure 4.44 compares the simultaneous removal in the presence and absence of oxygen on a Cu/AC adsorbent. It can be seen from the Figure that in the absence of oxygen, the presence of SO₂ did not result in any significant decrease in the NO breakthrough time on Cu/AC adsorbent. However, a high yield of NO (measured as the difference between influent and effluent NO concentration) was obtained. This yield was higher in comparison to the yield of NO that was obtained in the absence of SO₂. Interestingly, in the presence of O₂, a tremendous improvement in the NO removal performance was achieved and NO was completely removed for approximately 3 h with only 1 g of the adsorbent.
Figure 4.43 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Reduced Iron Impregnated Activated Carbon in the Presence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition. 400 ppm NO, 3000 ppm SO2, 5 % O2, bal N2; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
Figure 4.44 Simultaneous Removal of Sulfur Dioxide and Nitric Oxide on Reduced Copper Impregnated Activated Carbon in the Presence and Absence of Oxygen

[Test conditions: Bed height, 5.5 cm; Bed volume, 6.967 cc; Influent gas composition, 400 ppm NO, 3000 ppm SO$_2$, 5 % O$_2$, bal N$_2$; Residence time, 4 sec; Adsorption temperature, 125°C; Amount of adsorbent, 1 g]
4.7 Phase 7: Kinetic modeling

A very important aspect for any development of the process is the proper design of the adsorber and/or reactor. The objective of this phase was to develop a model to predict the adsorption of SO$_2$ theoretically and to develop a reaction mechanism for the reactive removal of NO on lignite and other lignite-derived adsorbents. In addition, a rate expression was also formulated to describe the removal of NO by lignite, char and activated carbon adsorbents.

4.7.1 Modeling and simulation of sulfur dioxide adsorption on lignite

In the literature (Ruthven, 1984), modeling of adsorption systems for various combinations of adsorbent and adsorbates are well documented. In order to develop a model which can predict theoretical breakthrough curves, one should have equations describing fluid phase and solid phase mass balances for the adsorbate along with the equation describing the adsorption equilibrium. The equation which can describe the fluid phase mass balance of the adsorbate for a fixed bed adsorption process is unique. It is known from the literature (Ruthven, 1984) that in the fixed bed adsorption process, the potential rate controlling phenomena include intraparticle diffusion, external film diffusion and actual surface diffusion processes. On the other hand, various adsorption equilibrium equations, which have been used in the literature, can be broadly classified as either linear or non-linear type. As our results showed that the higher adsorption of sulfur dioxide on lignite and lignite-derived char and activated carbon was achieved with lower influent concentrations, it was assumed that the adsorption of NO on these adsorbents was favorable. Consequently, the non-linear adsorption equation was the obvious choice. Ruthven et. al. (1974a, 1974b, 1975) reported a model which could successfully predicts the adsorption profile of ethane and ethene on zeolite adsorbent. The author assumed intraparticle diffusion of ethane and ethene as the rate controlling mechanism for adsorption and used a Langmuir type adsorption equation as the equilibrium isotherm. As zeolite and lignite-derived adsorbents (which were used in our work as the adsorbent) are both
microporous, Ruthven's model was adopted for the theoretical prediction of sulfur dioxide adsorption on lignite and lignite-derived adsorents after incorporating some simplifications. It is worth mentioning that, though zeolite and activated carbon are both microporous adsorbents, while zeolite is a well-defined crystalline material with narrow and uniform pore size, activated carbon is an amorphous substance with larger pores and a wider pore size distribution. Furthermore, from our previous studies on the adsorption of sulfur dioxide, it was observed that adsorption of sulfur dioxide was strongly dependent on the percentage of supermicropores and was weakly dependent of the particle size. Therefore, instead of intraparticle diffusion (as used by Ruthven et. al.), external film diffusion was considered as the rate controlling mechanism for the adsorption of sulfur dioxide on lignite.

For the isothermal adsorption of a single component from a dilute fluid mixture, the equations which define the concentration profile through the column and hence the breakthrough curve, may be written:

\[
V(\delta C/\delta Z) + (\delta C/\delta t) + (1-\epsilon)/\epsilon(\delta q/\delta t) = D_L(\delta^2 C/\delta Z^2) \quad (4.4)
\]

\[
(\delta q/\delta t) = k_f a (C-C^*) \quad (4.5)
\]

\[
q/q_a = (bC^*)(1+bC^*) \quad (4.6)
\]

with the appropriate initial and boundary conditions for the saturation of an initially adsorbate free column as follows:

\[
C(0,t) = C_0, \quad C(Z, Z/V) = 0, \quad q(Z, Z/V) = 0 \quad (4.7)
\]

Implicit in this formulation of the problem were the assumptions that equilibrium was governed by a Langmuir isotherm (Equation 4.6), and that the rate of mass transfer was controlled by external fluid film resistance (Equation 4.4). Using suitable manipulations of the variables (Garg and Ruthven, 1984), these equations were reduced to the following set of ordinary differential equations:
\[ \frac{d\phi}{d\tau} = \left(\frac{1}{\alpha}\right)(\phi - \psi) \]  
\[ \frac{d\psi}{d\tau} = (\phi - ((\psi - \lambda \psi)/(1 - \lambda \psi)) \]  

where,

\( b \) = Langmuir equilibrium constant
\( C \) = Adsorbate concentration in the fluid phase
\( C_0 \) = Adsorbate concentration in the influent gas mixture
\( C^* \) = Fluid phase adsorbate concentration in equilibrium with q
\( q \) = Average adsorbate concentration in a pellet
\( q_s \) = Saturation adsorbate concentration in Langmuir adsorption equation
\( k_f \) = External fluid film mass transfer coefficient
\( t \) = Time
\( V \) = Linear fluid velocity
\( Z \) = Distance measured from the bed inlet
\( \alpha = ((1 - \varepsilon)/\varepsilon) * (k_f a D_L)/V^2 \)
\( \varepsilon \) = Void fraction of the bed
\( \phi \) = Dimensionless fluid phase concentration \((C/C^*_0)\)
\( \psi \) = Dimensionless adsorbent phase concentration \((q/q_s)\)
\( \lambda = ((bC^*_0)/(1 + bC^*_0)) \)
\( \tau \) = Dimensionless time, \((k_f a t C^*_0/q_s)\)

Equation 4.8 and 4.9 were integrated for defined values \( \alpha \) of \( \lambda \) and \( \tau \) using a fourth-order Runge-Kutta routine. At this point what was unknown was the Langmuir adsorption equilibrium isotherm constant. To obtain the value of \( \lambda \) the following procedure was followed: value of \( \lambda \) was obtained by non-linear regression of \( C^*_0 \) and \( q_s \). While \( C^*_0 \) values were known from the sulfur dioxide adsorption experiments with lignite, \( q_s \) values were unknown. \( q_s \) corresponds to the amount of sulfur dioxide adsorbed up to saturation. Saturation of adsorbent corresponds to an
effluent concentration which is equal to the influent concentration. Generally, the value of $q_e$ is calculated from the static or equilibrium experiments in an ideal situation. As this information was not available, the value of $q_e$ was evaluated by integrating the experimental breakthrough curves generated for lignite at various combinations of the influent sulfur dioxide concentration ($C_i$) and residence time. Theoretically predicted breakthrough curves generated for various degrees of axial dispersion ($\alpha$) were subsequently matched with experimentally generated breakthrough profiles.

Figure 4.45 shows the effect of $\alpha$ for a specified value of $\lambda$. It can be seen from the Figure that in the case of high axial dispersion ($\alpha$), sulfur dioxide started leaking out of the bed early and took longer time to reach the influent sulfur dioxide concentration. On the other hand, for $\alpha = 1$, which was indicative of lower axial dispersion, the breakthrough time was longer and the shape of the breakthrough curve was steep.

Figure 4.46 shows the effect of $\lambda$ on the sulfur dioxide breakthrough profile on lignite. It can be seen from the Figure that a high value of $\lambda$ results in the longer breakthrough times as well as steeper breakthrough profiles as compared to the ones resulting from a lower value of $\lambda$. This was consistent with the fact that higher values of $\lambda$, which means more favorable adsorption of the adsorbate, should facilitate the transfer of adsorrate from the gas phase to the solid phase.

The experimental breakthrough curves obtained from sulfur dioxide adsorption experiments with lignite were subsequently matched with the theoretical ones. While, theoretical breakthrough curves were plotted against dimensionless time, experimental breakthrough curves were plotted against real time. Therefore, in order to match the experimental breakthrough curve with the theoretical one, experimental curve was shifted over the theoretical one. One typical match between theoretical and experimental breakthrough curve is shown in Figure 4.47. It can be seen from the Figure 4.45 and Figure 4.47 that lower value of axial dispersion ($\alpha$)
Figure 4.45 Effect of $\alpha$ (Index for Axial Dispersion in the Column) on Predicted Sulfur Dioxide Breakthrough Profile on Lignite for a Specified Value (0.7) of $\lambda$ (Index for Adsorption Equilibrium)

$[\alpha = \frac{1-\varepsilon}{\varepsilon}(k_{\text{atC}}/q_0)]$ values are shown as the legend whereas $\lambda = \frac{bC_0}{1+bC_0}$
Figure 4.46 Effect of $\lambda$ on Predicted Sulfur Dioxide Breakthrough Profile on Lignite for a Specified Value (1.0) of $\alpha$

$\alpha = (1-\varepsilon)/\varepsilon$ and $\lambda = (\beta C_0)/(1+\beta C_0)$ values are shown in the legend.
Figure 4.47 Sulfur Dioxide Breakthrough Curve on Lignite: Theoretical and Experimental Results

[Solid unconnected squares represent theoretical values generated from the simulation of the model. Empty squares connected by the solid line are the experimental sulfur dioxide concentration profile slid over the dimensionless time axis in order to match with the theoretical curve]
was more appropriate. The values of $\lambda$ and $\alpha$ obtained from this match were 0.7 and 1.0, respectively.

4.7.2 Derivation of rate models for the removal of nitric oxide by carbon-based adsorbents.

It was shown earlier that in addition to physical adsorption, nitric oxide also was removed by surface chemical reaction. Therefore, the theoretical models used to predict breakthrough of sulfur dioxide could not be used for the theoretical prediction of the nitric oxide breakthrough profiles. If one wishes to predict the breakthrough of nitric oxide through a bed of lignite, char or activated carbon adsorbent, the reaction terms also should be considered.

Generally, rate equations for any reaction kinetics are developed using either an empirical power law or a semi-empirical Langmuir-Hinshelwood-Hougen-Watson (LHHW) model. Both of these procedures use the steady-state conversion of the reactants. In the LHHW model, for tractability in the mathematical analysis and help in the theoretical understanding, it is customary to assume that one step in the reaction is rate-limiting or rate-controlling. This may be the rate of adsorption of one reactant, the rate of a surface reaction between adsorbed species, or the rate of desorption of a product. All the other steps are assumed to be in equilibrium with one another. The concept of a rate-controlling step can sometimes be confusing. Since all the processes occur in series under steady state conditions, they must all actually have the same rate. Furthermore, kinetic models developed under steady-state conditions are not suitable to describe the dynamics of the adsorbent and the reactor. The reason is that the model parameters determined under stationary conditions are in general lumped. An example is the widely used Langmuir-Hinshelwood equation to describe heterogeneous catalytic kinetics. Consider a simple irreversible overall reaction:

\[ \text{A}_1 + \text{*} \rightarrow \text{A}_1^* \]  \hspace{1cm} (4.10)

\[ \text{A}_1^* \rightarrow \text{A}_2 + \text{*} \]  \hspace{1cm} (4.11)
taking place in two steps involving empty sites $A_1^*$ and occupied sites $A_1^*$. The condition of steady state and the balance of active sites yield the following equation for the transformation rate of $A_1$.

$$-R_1 = \frac{(a^*C_1^*)}{(1+b^*C_1^*)} \quad (4.12)$$

where,

$-R_1 = \text{rate of disappearance of the reactant } A_1$

$a, b = \text{constants}$

$C_1 = \text{concentration of reactant } A_1$

This kinetic model has two lumped parameters which are $a$ and $b$. The constant, $a$, depends on the rate constant of the surface reaction, the total concentration of the active centers on the catalyst and the catalyst mass per unit reactor volume. The other constant $b$ depends on the concentration of sites occupied by the reactant $A_1$. Under steady state conditions, it is very difficult to get information on the value of the individual rate constants for the surface reaction and adsorption processes.

At unsteady state and the given feed concentration and space time, the conversion in a reactor depends on $a$ and $b$. The transient behavior is also strongly influenced by the individual rate constants and the concentration of active site.

Based on the information obtained from the experiments regarding the removal of NO by lignite and lignite-derived adsorbents and using a recently developed unsteady-state approach (Renken, 1990), a rate law has been developed which can correlate both unsteady-state and steady-state conversion of nitric oxide. Details will now be discussed here.
4.7.2.1 Reaction mechanism for the removal of NO removal by lignite and lignite-derived adsorbents

It can be seen from the literature that activated carbon surfaces contain surface oxides which are either present due to the inherent nature of the adsorbents or can be formed due to reaction of the carbon surface with oxygenated reactants such as nitric oxide and oxygen. It has also been observed from our experiments that effluent nitric oxide concentrations from the adsorber did not reach the influent nitric oxide concentration over the time period studied. This was attributed to the removal of nitric oxide by surface chemical reaction. This assumption was further substantiated when the yield of NO due to reaction increased due to the presence of oxygen. Therefore, based on the literature and the results concerning adsorptive and reactive removal of NO from previous phases, it was possible to develop a reaction mechanism for the removal of NO on lignite, char and activated carbon. This was given as follows:

\[
\begin{align*}
\text{NO} + \text{L (C-Oxides)} & \rightarrow \text{NO-L (C-Oxides)} \quad (4.13) \\
\text{NO-L (C-Oxides)} & \rightarrow \text{NO}_2 \quad (4.14) \\
\text{O}_2 + \text{C} & \rightarrow \text{C-oxides} \quad (4.15)
\end{align*}
\]

where, L and NO-L indicated empty and occupied sites, respectively.

4.7.2.2 Rate modelling

It was mentioned earlier that there was no difference in the breakthrough time of NO on lignite, char and AC eventhough the microporosity of AC and char was much higher than lignite. To describe the observed breakthrough profile of NO over lignite, char and activated carbon, adsorption of NO on the adsorbent surface was assumed. For very fast adsorption processes, the surface concentration of the adsorbate can be assumed to be in equilibrium with the gas phase concentration at any
instant. With the above-mentioned assumptions, the following mathematical model was developed.

\[ \frac{dC}{dt} = \frac{(K_v \cdot C)}{(1 + PK \cdot C)} \]  \hspace{1cm} (4.16)

\[ PK = \frac{K_s}{(K_c \cdot m_c / V_r + K_d)} \]  \hspace{1cm} (4.17)

where,

\begin{align*}
K_s & = \text{rate of adsorption} \\
K_c & = \text{rate of surface reaction} \\
m_c & = \text{weight of the catalyst} \\
K_d & = \text{rate of desorption} \\
V_r & = \text{volume of the reactor} \\
K_v & = \text{volumetric rate constant}
\end{align*}

As a rate law of this kind has never been reported before, the approximate magnitudes of the different parameters were not known; therefore, these were determined by adaptation of theoretically predicted to experimentally generated breakthrough profiles for NO. For this purpose, a computer program was developed which was able to solve the ordinary differential equation.

To generate theoretical values of the effluent concentrations of NO from the adsorber, it was further assumed that the rate of desorption was negligible. This assumption was not bad when viewed against the fact that the adsorption of nitric oxide on lignite and lignite-derived adsorbents were the highly favorable type.

Theoretical values of the effluent NO concentrations were generated for different combinations of three constants: \(K_s\), rate of adsorption and \(K_c\), rate of surface reaction. The values for the rest of the parameters were known from the experiments. The effect of various parameters such as \(K_s\), \(K_c\), and residence time \(\tau\) are shown in Figures 4.48, 4.49 and 4.50, respectively.

It can be seen from Figure 4.48 that a decrease in \(K_s\) value not only increased breakthrough time but also decreased the mid-point slope. On the other hand,
Figure 4.48 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Rate Constant of Adsorption, $K_a$
Figure 4.49 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Rate Constant of Surface Reaction, $K_C$
Figure 4.50 Dynamic Behavior of the NO Removal After Stepwise Increase of Influent Concentration for Different Values of Residence Time, $\tau$
decrease in $K_c$ (Figure 4.49) resulted in longer NO breakthrough times. These two observations can be explained as follows: It was observed from previous experiments that NO adsorption is kinetically controlled and surface reaction plays a major role in the NO adsorption process. Therefore, due to a decrease in rate of adsorption (low $K_s$) and surface reaction ($K_c$), longer times would be required to saturate the adsorption capacity of the adsorbent.

Figure 4.50 shows the effect of residence time on the NO breakthrough profile. It can be seen from the Figure that residence time did not have a very significant effect on the NO breakthrough time and the slope of the breakthrough curve. These observations were subsequently used during matching of the experimental and theoretical NO breakthrough profiles.

Figure 4.51 compares the theoretically predicted NO breakthrough with those of experimentally generated ones for char and activated carbons, respectively. It can be seen from the Figure that the model successfully correlated with the experimental observation. However, one can raise questions about the inability of the model to correlate the oscillation of the NO breakthrough profiles, particularly in the case of activated carbon. It should be mentioned here that the theoretical model did not consider the oscillations in the breakthrough curves because of the inherent complexity. In the literature, oscillations have been attributed to the presence of different kinds of active sites. It is also known that lignite used in this study contained appreciable amount of inorganic material. The percentage of inorganic material increased progressively during the course of carbonization and activation. Therefore, activated carbon contained significant amounts of metal species which created different types of active centres and consequently resulted in the oscillations in the breakthrough profiles. In the literature, oscillations of these types have never been reported for NO removal process on activated carbon adsorbents. The assumption of the presence of the oscillations due to the existence of different kinds of active centers was further substantiated when the oscillations became worse due to the impregnation of additional amounts of metal oxides into the activated carbon support. In the case of
Figure 4.51 Nitric Oxide Breakthrough Curves on Char and Activated Carbon: Theoretical and Experimental Results

[Solid lines in the plot represent theoretical values. Unconnected solid circles represent experimental NO breakthrough curve. Squares are for activated carbon]
metal-impregnated activated carbons, rate equations based on the above mentioned unsteady-state approach, were not developed. This was due to the inherent complexity of the systems and unavailability of the necessary data.
4.8 Non-selective catalytic reduction of NO using methanol as a reductant

Currently, there are a number of NO control technologies involving catalytic NO conversion (reduction). Usually, these are performed in the presence of reductants such as ammonia (NH₃), hydrocarbons (CₓHᵧ), oxygenated hydrocarbons, hydrogen (H₂) and carbon monoxide (CO) for higher efficiency. However, it is very important that these reductants be effective in NO reduction in an oxygen rich environment since oxygen is always present where NO is produced. It is also desirable that they do not pose any storage, transportation or handling problems.

There is an on-going research program in our laboratory dealing with the production of hydrogen at low temperatures by methanol decomposition or methanol steam-reforming. It has been shown by Idem et. al. (1994) that a Mn-promoted Cu-Al co-precipitated catalyst is very efficient and effective for this purpose.

There are conflicting reports in the literature concerning the effectiveness of the reductants such as H₂ and CH₃OH in the reduction of NO. This may be attributed to the difference in the types of catalysts used by various workers and the little information available in the literature on the nature of these reductants at the time of NO reduction. Some of the catalysts which have been effective for the NO reduction, contain catalyst components such as copper species (as in Cu-ZSM-5, CuO/Al₂O₃, Cu-Y Zeolite), manganese species (as in Mn-ZSM-5), and alumina (as in Fe₂O₃/Al₂O₃, CuO/Al₂O₃, V₂O₅/Al₂O₃). Since a Mn-promoted Cu-Al co-precipitated catalyst was effective for hydrogen production from methanol, and also contained various forms of Cu, Mn and Al species, it was decided to perform a preliminary evaluation of its performance for NO reduction. This reduction was carried out simultaneously with either the methanol decomposition or methanol-steam reforming process so that they could supply the reductants such as H₂, CH₃OH, CH₄ and CO (either in the nascent form or molecular form) needed for NO reduction. These species were found to be produced (Idem et. al., 1994) as reaction intermediates or products during the production of hydrogen from methanol. Thus, methanol acted as
their chemical storage, in addition to a possible role as reductant. As previously mentioned, NO reduction experiments were conducted in the presence and absence of oxygen, and methanol/water molar ratios of 1/0, 1/1 and 1/3. Nitric oxide (NO) was used in all the experiments to represent NO since it constitutes the major proportion of the NO.

Table 4.11 and 4.12 show the NO conversions obtained as a function of reaction temperature and methanol/water molar ratio for test runs conducted in the presence and absence of oxygen, respectively. In the Table 4.11, it can be seen that in the absence of oxygen, NO conversion decreased with a decrease in the reaction temperature, specially at low methanol/Water molar ratios. NO conversion also decreased with a decrease in the methanol/water molar ratio, specially at low reaction temperatures. At the reaction temperature of 300°C and for all three methanol/water molar ratios, NO was reduced completely to nitrogen. To the best of our knowledge, this is the first time methanol has been used to successfully reduce NO to nitrogen. The overall reduction can be represented by the following equation:

\[ 6\text{NO} + 2\text{CH}_3\text{OH} = 3\text{N}_2 + 4\text{H}_2\text{O} + 2\text{CO}_2 \]

Table 4.11 shows that at 250°C, NO conversion was 100 mole % or nearly 100 mole %. However, at 200°C, NO conversion decreased with decreasing methanol/water molar ratio. Low conversions at low methanol/water molar ratios and reaction temperatures can be explained as follows. It was mentioned earlier that the methanol/water mixture was fed into the reactor at the same volumetric feed rate for all experiments. This means that the lower the methanol/water molar ratio, the lower the actual amount of methanol that is fed into the reactor. This situation becomes critical at low reaction temperatures for two reasons. Firstly, the amount of reductant (such as H₂, CO, CH₄) available for NO reduction may be less than what is stoichiometrically needed, since methanol conversion is low at low temperatures (endothermic reaction). Secondly, since NO reduction is an endothermic reaction it will be affected by low temperature in the same manner as methanol conversion.
Table 4.11 Reduction of Nitric Oxide Using Methanol As the Reductant in The Absence of Oxygen

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>Nitric oxide (NO) reduction efficiency in the absence of oxygen (O₂), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH:H$_2$O Molar ratio</td>
<td>Reduction temperature</td>
</tr>
<tr>
<td>1:0</td>
<td>100</td>
</tr>
<tr>
<td>1:1</td>
<td>100</td>
</tr>
<tr>
<td>1:3</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.12 Reduction of Nitric Oxide Using Methanol As the Reductant in The Presence of Oxygen

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>Nitric oxide (NO) reduction efficiency in the presence of oxygen (O₂), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH:H$_2$O Molar ratio</td>
<td>Reduction temperature</td>
</tr>
<tr>
<td>1:0</td>
<td>100</td>
</tr>
<tr>
<td>1:1</td>
<td>57</td>
</tr>
<tr>
<td>1:3</td>
<td>*</td>
</tr>
</tbody>
</table>

* Not performed
A comparison of Tables 4.11 and 4.12 shows that the conditions for \( \text{H}_2 \), CO and \( \text{CH}_4 \) production from methanol are similar to those for NO reduction. Thus, it appears that \( \text{H}_2 \), CO and \( \text{CH}_4 \) species are directly responsible for NO reduction.

In the case of experiments performed in the presence of oxygen, Table 4.12 shows that NO conversion decreased drastically with a decrease in both the reduction temperature and the methanol/water molar ratio. As in the case of experiments in the absence of oxygen, low NO conversion at low reduction temperatures and methanol/water molar ratios was attributed to the effect of low temperature on methanol and NO conversions, and the small amounts of methanol actually fed to the reactor at low methanol/water molar ratios. Results from Table 4.11 and 4.12 show that there was a deterioration in the NO conversions in experiments conducted in the presence of oxygen when compared with those for experiments conducted in the absence of oxygen. This deterioration in performance indicates that using the Mn-promoted Cu-Al co-precipitated catalyst in conjunction with the methanol decomposition or methanol steam-reforming process, the reductants generated (i.e., \( \text{H}_2 \), CO and \( \text{CH}_4 \)) are not selective for NO reduction alone. NO has to compete for these reductants with oxygen. These results show that with the catalyst, the reductants appear to be more reactive for oxygen than for NO, thus resulting in a low or no conversion of NO.
5. Conclusions

5.1 Phase 1: Preliminary work

It has been shown that the adsorbent degassing temperature has tremendous influence on adsorption isotherms and, consequently, on the micropore surface area, volume, pore size and pore size distributions of lignite.

5.2 Phase 2: Preparation of char and activated carbon from lignite and their characterization

a. Using statistical and experimental approaches, it has been shown that SO₂ adsorption performance improves with decrease in residence time and increase in influent SO₂ concentration.

b. SO₂ adsorption capacity did not improve due to carbonization of lignite. However, a large improvement in SO₂ adsorption capacity, approximately 175%, was achieved after the char was activated with steam at 650°C.

c. Steam activated carbons exhibited higher SO₂ adsorption capacities as compared to carbon dioxide activated carbons.

d. The SO₂ adsorption capacity depended significantly on the fraction of the supermicropores (10-20Å) present in the adsorbents.

5.3 Phase 3: Preparation and characterization of metal-impregnated activated carbon

a. Impregnation of activated carbon with iron resulted in the deposition of iron on the surface of the granule. Calcination of iron-impregnated activated carbon
adsorbents resulted in the partial migration of the iron oxide species into the ultramicropore system.

b. Impregnation of activated carbon with Cu, Co and Ni, on the other hand, resulted in the introduction of the active metal species into the supermicropore system.

5.4 Phase 4: Adsorptive and reactive removal of sulfur dioxide

a. In the absence of oxygen, only the activated carbon adsorbent, impregnated with iron oxide additive, resulted in a significant improvement in the SO$_2$ adsorption capacity of activated carbon adsorbent.

b. In the presence of oxygen, only copper impregnated activated carbon adsorbent exhibited a large improvement in the SO$_2$ removal performance.

c. In the presence of oxygen, the yields of SO$_2$ for metal-impregnated activated carbons were significantly higher than those for non-impregnated activated carbons.

5.5 Phase 5: Adsorptive and reactive removal of nitric oxide by lignite and various lignite-derived adsorbents

a. In the absence of oxygen, lignite and lignite-derived char and activated carbons exhibited low NO adsorptive removal capacity. However, the overall NO removal efficiency for all adsorbents became higher when the reactive NO removal component (yield) was taken into consideration. The NO yields for these adsorbents increased in the order lignite < char < activated carbon.

b. In the absence of oxygen, there was no difference in the NO removal performance between activated carbon (AC) and unreduced iron impregnated activated carbon (Fe/AC). However, there was a tremendous improvement in the NO removal performance (400%), in terms of NO breakthrough time, when Fe/AC adsorbent was reduced by hydrogen.
c. In the presence of oxygen, there was significant improvement in the overall NO removal efficiency with reduced Cu/AC, Co/AC and Ni/AC adsorbents over that of AC.

5.6 Phase 6: Simultaneous removal of sulfur dioxide and nitric oxide
a. In the absence of oxygen, the presence of SO\(_2\) improved the NO removal efficiency of metal-impregnated activated carbons. However, in contrast, the SO\(_2\) removal efficiency decreased due to the presence of NO.
b. In the presence of oxygen, the improvement in the NO removal efficiency was higher than in the absence of oxygen, while the removal efficiency of SO\(_2\) deteriorated.
c. In the presence of oxygen, a tremendous improvement in NO removal performance was achieved with Cu/AC and Fe/AC adsorbents.

5.7 Phase 7: Modeling and simulation of SO\(_2\) adsorption and NO reaction
a. A model that is capable of predicting the SO\(_2\) breakthrough profile on lignite has been developed.
b. A model capable of predicting both the steady-state and transient yield of NO over char and activated carbon has been developed for the first time.

5.8 Phase 8: Catalytic reduction of NO by in-situ decomposition and steam reforming of methanol
a. In the absence of oxygen, nitric oxide was completely reduced by methanol over a Mn-promoted co-precipitated Cu-Al catalyst even at temperatures as low as 200°C.
b. In the presence of oxygen, methanol also reacted with the oxygen rendering the process non-selective for NO reduction.
6. RECOMMENDATION

Results from the present study have shown an improvement in the $\text{SO}_2$ and NO adsorption performance of metal-impregnated activated carbon adsorbents over that of activated carbon adsorbent. For this reason, all the recommendations apply to the metal-impregnated activated carbon adsorbents, unless specified.

[1] The large improvement in the $\text{SO}_2$ and NO removal performances were achieved with metal-impregnated activated carbon adsorbents containing metal in concentrations as low as 1 wt%. For this reason, it is recommended that studies on $\text{SO}_2$ and NO removal be conducted with metal-impregnated activated carbon adsorbents containing higher amounts of metal in order to determine whether this will lead to better performance.

[2] In the current study, it was observed that high NO removal was possible with metal-impregnated activated carbons even in the presence of 6.5% oxygen. This phenomenon was attributed to the oxidation of NO to $\text{NO}_2$ over metal-impregnated activated carbon catalysts. This can be used for the removal of NO from power plant flue gases. It appears that not much work has been done in this area. It is therefore recommended that a detailed study be carried out to determine the operating conditions necessary for success of such a process.

[3] Modeling of NO over lignite, char and activated carbon adsorbents was successful. However, the model can not account for the oscillations in the breakthrough curves. These oscillations were attributed to the presence of different types of active centers in the adsorbent. It is therefore recommended that more work be done on the detection of different active site and determination of their
concentrations; these concentrations can then be used to generate a more rigorous model.

[4] A large improvement in the SO$_2$ and NO removal performances were achieved with metal-impregnated activated carbon adsorbents in the presence of oxygen. However, actual flue gas also contains large quantities of H$_2$O. It has been reported in the literature that the presence of H$_2$O can influence the removal of SO$_2$ and NO to a great extent. It is therefore recommended that further studies be carried out to determine the effect of H$_2$O on the SO$_2$ and NO removal performances of the metal-impregnated activated carbons.

[5] In any adsorptive and catalytic process, the working capacity, i.e., the average capacity that can be maintained after several adsorption-desorption cycles, is an important parameter. It is therefore recommended that further studies be carried out in order to determine the regeneration characteristics of the metal-impregnated activated carbons.

[6] In this study, it was observed that lignite can adsorb an appreciable quantity of NO in the presence of oxygen. This could be used for the NO removal from a small facility. For example, in power plants where lignite is burnt in order to produce power and the formation of NO is not very high with respect to the emission limit, a small stream of the flue gas can be taken out from the main stream and routed through a lignite bed. After the adsorption cycle, lignite can be charged in the boiler along with the other fresh lignite. Studies should be conducted to determine the feasibility of such a process.
7. References


Iwamoto, M., "Copper Ion-Exchanged Zeolites as Active Catalysts for Direct Decomposition of Nitrogen Monoxide", p327, Proceedings of The International Symposium on the Chemistry of Microporous Crystals, Tokyo, (June, 1990)


Kerkhof, F.M.G. van den, "Selective Catalytic Reduction Of NO$_x$ From Flue gas" (in Dutch), I2-Processtechnologie, 11, 35, (1986).


Takagi, M., Kawai, T., Soma, M., Onishi, T. and K. Tamaru, "The Mechanism of the Reaction Between NO\textsubscript{2} and NH\textsubscript{3} on V\textsubscript{2}O\textsubscript{5} in the Presence of Oxygen", J. Catal., 50, 441, (1977).


Wong, W.C. and K. Nobe, "Reduction of NO with NH\textsubscript{3} on Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}-supported Metal Oxide Catalysts", Ind. Eng. Chem. Prod. Res. Dev., 25, 179, (1986).


APPENDIX A : SAMPLE CALCULATIONS

All the results obtained in this work are stored in floppy disks. Those are available on request from the address given below:

Dr. N.N. Bakhshi

"Catalysis and Chemical Reaction Engineering Laboratory"

Department of Chemical Engineering, University of Saskatchewan.

110 Science Place, Saskatoon, SK. S7N 5C9

<table>
<thead>
<tr>
<th>Component</th>
<th>TCD</th>
<th>FID</th>
<th>Corrected FID &amp; TCD combined</th>
<th>Weight %</th>
<th>Molecular weight</th>
<th>Mole equivalent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.3879</td>
<td>75.82</td>
<td>92.95</td>
<td>61.57</td>
<td>16</td>
<td>3.848</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>3.25</td>
<td>3.08</td>
<td>2.04</td>
<td>28</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>2.28</td>
<td>2.44</td>
<td>1.61</td>
<td>30</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>4.09</td>
<td>3.86</td>
<td>2.56</td>
<td>42</td>
<td>0.061</td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>1.03</td>
<td>1.05</td>
<td>0.70</td>
<td>44</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>C₄'S</td>
<td>2.45</td>
<td>2.28</td>
<td>1.51</td>
<td>57</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>C₅'S</td>
<td>3.42</td>
<td>3.50</td>
<td>2.32</td>
<td>71</td>
<td>0.033</td>
<td></td>
</tr>
<tr>
<td>C₆⁺</td>
<td>5.84</td>
<td>5.98</td>
<td>3.96</td>
<td>83</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.0613</td>
<td>14.69</td>
<td>9.73</td>
<td>28</td>
<td>0.347</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0882</td>
<td>21.15</td>
<td>14.01</td>
<td>44</td>
<td>0.318</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000</td>
<td>0.00</td>
<td>0.00</td>
<td>2</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>150.98</td>
<td>100.00</td>
<td>4.824</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Component</td>
<td>Mole fraction</td>
<td>Gas Density at STP (g/mL)</td>
<td>Volume, mL</td>
<td>Gas composition (wt % of the feed)</td>
<td>weight (g)</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------------</td>
<td>---------------------------</td>
<td>------------</td>
<td>----------------------------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.798</td>
<td>0.000654</td>
<td>509.17</td>
<td>6.01</td>
<td>0.333</td>
<td></td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.015</td>
<td>0.00115</td>
<td>9.63</td>
<td>0.20</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.011</td>
<td>0.00123</td>
<td>7.13</td>
<td>0.16</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.13</td>
<td>0.00172</td>
<td>8.06</td>
<td>0.25</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0033</td>
<td>0.0018</td>
<td>2.10</td>
<td>0.07</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>C₄'S</td>
<td>0.0055</td>
<td>0.00233</td>
<td>3.51</td>
<td>0.15</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>C₅'S</td>
<td>0.0068</td>
<td>0.0029</td>
<td>4.32</td>
<td>0.23</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>C₆'</td>
<td>0.0099</td>
<td>0.00339</td>
<td>6.31</td>
<td>0.39</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.0720</td>
<td>0.00115</td>
<td>45.98</td>
<td>0.96</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0660</td>
<td>0.0018</td>
<td>42.12</td>
<td>1.37</td>
<td>0.076</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.0000</td>
<td>8.8 x 10⁻⁵</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1.0000</td>
<td></td>
<td>638.32</td>
<td>9.84</td>
<td>0.541</td>
<td></td>
</tr>
</tbody>
</table>

**Procedure of calculation**

**From Chromatograph A:**

1. In column 1 in Table I.1, the (CH₄ area %)/Correction factor for CH₄ is written i.e., (13.811/35.7) = 0.0387

2. Similarly for CO₂, the corresponding value of CO₂ from the same chromatogram is given by (4.236/48.0) = 0.08825 and is written in column 1.
From Chromatogram B:

3. The ratio of CO/CH\textsubscript{4} from the corresponding peaks at 9.95 and 14.4 minutes is taken to be (4.333/23.331) = 0.1865. Incorporating this value in values obtained previously for CH\textsubscript{4} and CO\textsubscript{2}, the corresponding area % for CO would be (0.1865*13.811) = 2.576. Dividing this value for CO by its correction factor 42, the corresponding value detected for CO is (2.576/42) = 0.0613. This value is also put in column 1.

From Chromatogram C:

The ratio of H\textsubscript{2} to CH\textsubscript{4} the ratio of uncorrected area %'s is given by values for peaks at 1.85 and 3.81 minutes, i.e., (62.165/3.076) = 20.209. Multiplying this ratio by the original area % of CH\textsubscript{4} from Chromatogram A: (20.209*13.811) = 279.1065.

This value is the uncorrected TCD value for H\textsubscript{2} yield, which has to be divided by the correction factor for H\textsubscript{2}: (279.1065/500.00) = 0.5582. This value is put in column 1 of Table I.1 for H\textsubscript{2}.

The above mentioned values in column 1 represent the weight ratios of all the gases detected by the thermal conductivity detectors (TCD).

From Chromatogram D:

In column 2 the values obtained from the FID run for the hydrocarbon gases are given. These values represent the weight distribution of hydrocarbon gases.

Using the ratio of all the gases detected by the TCD runs to the CH\textsubscript{4} weight yield, all relative weight yields of gases are presented together in column 3. The FID values are also multiplied by their correction factors, which were determined by using a standard hydrocarbon gas mixture with the same FID system. These correction factors were as follows:

218
\[ \begin{align*}
\text{CH}_4 & \quad 1.226 \\
\text{C}_2\text{H}_4 & \quad 0.984 \\
\text{C}_2\text{H}_6 & \quad 1.069 \\
\text{C}_3\text{H}_6 & \quad 0.944 \\
\text{C}_3\text{H}_8 & \quad 1.019 \\
\text{C}_4\text{S} & \quad 0.931 \\
\text{C}_5\text{S} & \quad 1.023 \\
\text{C}_6 & \quad 1.023
\end{align*} \]

Knowing the weight % of the gases (column 4) and their molecular weight (column 5), mole equivalent (column 6) and mole fraction (column 7) can be determined. Column 8 gives the gas density of all the gases at standard conditions. The total volume gas collected is known from the total volume of gas collected in the graduated cylinders and/or passed through the wet test meter. Then the volumetric gas distribution is determined using information in column 7 and the total volume (6500 mL) of gas collected.

Column 11 gives the weight of the gas components calculated from columns 8 and 9. Column 10 gives the gas composition as weight % of the feed.

Once the volume of \( \text{N}_2 \) carrier is determined, it is subtracted from the total of 6500 mL, giving 638.32 mL as the total volume of pyrolysis gas produced from 5.5 g of lignite coal at 600°C.
### Gas Chromatograms (continued)

#### C:

**STOP**

**RUN # 99**

<table>
<thead>
<tr>
<th>AREA</th>
<th>RT</th>
<th>AREA TYPE</th>
<th>AR/MI</th>
<th>AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>1622400</td>
<td>PB</td>
<td>0.496</td>
<td>62.16</td>
</tr>
<tr>
<td>2.33</td>
<td>2332340</td>
<td>PB</td>
<td>0.118</td>
<td>22.27</td>
</tr>
<tr>
<td>2.20</td>
<td>206331</td>
<td>BP</td>
<td>0.159</td>
<td>0.79</td>
</tr>
<tr>
<td>3.20</td>
<td>137168</td>
<td>PV</td>
<td>0.125</td>
<td>0.25</td>
</tr>
<tr>
<td>3.81</td>
<td>892346</td>
<td>VB</td>
<td>0.056</td>
<td>1.87</td>
</tr>
<tr>
<td>4.81</td>
<td>11340</td>
<td>PH</td>
<td>0.333</td>
<td>0.43</td>
</tr>
</tbody>
</table>

**TOTAL AREA** = 2589700

**MULT Factor** = 1.0000E+00

---

#### D:

[Graphical data and analysis related to the chromatograms]
Appendix B: Gas Chromatographic Analysis Conditions

[1] Analysis of Nitric Oxide alone:

[a] Run Parameters:

ZERO = 0
ATT 2^ = 0
CHT. SP. = 1.0
AR. REJ = 0
THRSH = 0
PK. WD = 0.04

[b] Time Table Events:

0.00 TCD SENS. = LOW
0.01 VALVE 2 = ON
2.00 TCD SENS. = HIGH
2.050 ZERO = 0
2.100 ATT ^2 = -4
2.100 THRSH = -4
5.000 STOP

[c] Various Temperatures used:

Oven temperature, 30°C; auxiliary temperature, 100°C; detector temperature, 165°C.
[2] Analysis of Nitric Oxide in the presence of sulfur dioxide:

[a] Run Parameters:
ZERO = 0
ATT 2\(^\wedge\) = 0
CHT. SP. = 1.0
AR. REJ = 0
THRSH = 0
PK. WD = 0.04

[b] Time Table Events:
0.00 TCD SENS. = LOW
0.01 VALVE 2 = ON
4.500 TCD SENS. = HIGH
4.525 ZERO = 0
4.550 ATT \(^\wedge\)2 = -4
4.550 THRSH = -4
5.550 THRSH = -2
7.550 THRSH = 0
11.000 STOP

[c] Various Temperatures used:
Oven temperature programming parameters were as follows: initial temperature of the oven, 25\(^\circ\)C; initial time, 5.50 min; temperature program rate, 40\(^\circ\)C; final temperature, 105\(^\circ\)C; auxiliary temperature, 100\(^\circ\)C; detector temperature, 165\(^\circ\)C.
APPENDIX C: Computer Program

COMPUTER SIMULATION OF ADSORPTION-REACTION SYSTEM
SUBMITTED BY GOUTAM CHATTOPADHYAYA

******************************************************************************

MAIN BODY OF THE PROGRAM

******************************************************************************

* HOUSEKEEPING SECTION

******************************************************************************

OPEN(UNIT=12,FILE="REACT01.OUT",STATUS="NEW")

******************************************************************************

* INITIATION SECTION

******************************************************************************

100 FORMAT(1H1,1E8.4)

DIMENSION DTA(15)
PRINT*, 'ENTER THE VALUE OF DSA'
ACCEPT*, DSA
PRINT*, 'ENTER THE VALUE OF KC'
ACCEPT*, KC
PRINT*, 'ENTER THE VALUE OF LAMBDA'
ACCEPT*, LAMBDA
PRINT*, 'ENTER THE VALUE OF MC'
ACCEPT*, MC
PRINT*, 'ENTER THE VALUE OF VR'
ACCEPT*, VR
PRINT*, 'ENTER THE VALUE OF KD'
ACCEPT*, KD
PRINT*, 'ENTER THE VALUE OF TAU'
ACCEPT*, TAU
PRINT*, 'ENTER THE VALUE OF CO'
ACCEPT*, CO
PRINT*, 'ENTER THE VALUE OF ALPHA'
ACCEPT*,ALPHA
DO 8 J=1,2
ALPHA=(KC*LC*MC/VR)
LAMBDA=(KA/(KC*MC/VR)+KD))
DS=DSA
*
DERIVATIVE SECTION
7
DX=(ALPHA*LAMBDA*TAU*X/(1.+LAMBDA*X))
IF(X.GE.0.05) STP=0.
CALL PRNTF(5.0,60.0,NF,X,S,DX,DS,C,0.,0.,0.,0.,0.)
CALL PRNTF(5.,60.,NF,S,T,DS,DT,0.,0.,0.,0.,0.,0.,0.)
GO TO (5,8),NF
********************************************************************************

* INTEGRATION SECTION

********************************************************************************
CALL SIMPSN AREA,DUMMYF,XMIN,XMAX,N
5
CALL INTI(S,DS,4)
CALL INT(X,DX)
CALL INT(H,DH)
IF(ABS(E).LT.0.1)STOP
HI=HI-E*0.4
GO TO 7
8 CONTINUE
END

********************************************************************************

SUBROUTINES REQUIRED FOR INTEGRATION

********************************************************************************
SUBROUTINE INTI(TD,DTD,IOD)
COMMON/CINT/T,DT,JS,JN,DXA,XA,IO,JS4
DIMENSION DXA(500),XA(500)
IO=IOD
JN=0
GO TO (6,5,1,1),IO
6
JS=2
GO TO 7
5
JS=JS+1
IF(JS.EQ.3)JS=1

IF(JS.EQ.2)RETURN
7  DT=DTD
3  TD=TD+DT
T=TD
RETURN
1  JS4=JS4+1
   IF(JS4.EQ.5)JS4=1
   IF(JS4.EQ.1) GO TO 2
   IF(JS4.EQ.3) GO TO 4
   RETURN
2  DT=DTD/2.
   GO TO 3
4  TD=TD+DT
   DT=2.*DT
   T=TD
   RETURN
END

SUBROUTINE INT(X,DX)
COMMON/CINT/T,DT,JS,JN,DXA,XA,IO,JS4
DIMENSION DXA(500),XA(500)
JN=JN+1
GO TO (9,8,3,3),IO
9  X=X+DX*DT
   RETURN
8  GO TO (1,2)JS
1  DXA(JN)=DX
   RETURN
2  X=X+(DX-DXA(JN))*DT/2.
   RETURN
3  GO TO (4,5,6,7), JS4
4  XA(JN)=DX
    DXA(JN)=DX
    X=X+DX*DT
    RETURN
5  DXA(JN)=DXA(JN)+2.*DX
    X=XA(JN)+DX*DT
    RETURN
6  DXA(JN)=DXA(JN)+2.*DX
    X=XA(JN)+DX*DT
    RETURN
7  DXA(JN)=(DXA(JN)+DX)/6.
    X=XA(JN)+DXA(JN)*DT
    RETURN
END

C SUBROUTINE TRAPZD(FUNC,A,B,S,N)
C IF(N.EQ.1)THEN
C S=0.5*(B-A)*(FUNC(A)+FUNC(B))
C IT=1.
C ELSE
C TNM=IT
C DEL=(B-A)/TNM
C X=A+0.5*DEL
C SUM=0.
C DO 11 J=1,IT
C SUM=SUM+FUNC(X)
C X=X+DEL
C 11 CONTINUE
C S=0.5*(S+(B-A)*SUM/TNM)
C IT=2*IT
C ENDIF
C RETURN
C END
C SUBROUTINE DYDX

**********************************************************************

C SUBROUTINE FOR PRINTING

**********************************************************************

SUBROUTINE PRNTF(PRI,FNR,NF,A,B,C,D,E,F,G,O,P,Q)
COMMON/CINT/T,DT,JS,JN,DXA,XA,IO,JS4
COMMON/CPR/NPR
DIMENSION DXA(500),XA(500)
100 FORMAT(10E12.5)
NPR=0.
IF(TPRNT.LT.PRI) GO TO 4
IF((T.GE.FNR-DT/2.).AND.(JS4.EQ.4)) GO TO 6
IF((T.GE.TPRNT-DT/2.).AND.(JS4.EQ.4)) GO TO 5
RETURN
4 NF=1
5 TPRNT=TPRNT+PRI
8 PRINT 100,A,B,C,D,E,F,G,O,P,Q
NPR=1
RETURN
6 T=0.
TPRNT=0.
NF=2
DO 7 J=1,500
7 $XA(J)=0.$
GO TO 8
END
C SUBROUTINE PRNTRS(IS,A,B,C,D,E,F,G,O,P,Q)
C COMMON/CPR/NPR
C 100 FORMAT(10F10.5)
C IF(NPR.EQ.1)GO TO 5
C RETURN
C 5 PRINT 100,A,B,C,D,E,F,G,O,P,Q
C IF(IS.EQ.1)PRINT 100
C RETURN
C END
C*****************************************************************************
C SUBROUTINE TO ESTIMATE FUNCTION
C*****************************************************************************
C SUBROUTINE FUN1(T,N,AT,AQ)
C FUNCTION FUN1(A,N,X,Y)
C DIMENSION X(12),Y(12)
C IF(A-X(1)) 5,5,6
C 6 IF(A-X(N)) 1,2,2
C 2 FUN1=Y(N)
C RETURN
C 5 FUN1=Y(1)
C RETURN
C 1 DO 3 I=2,N
C IF (A.LT.X(I)) GO TO 4
C 3 CONTINUE
C 4 FUN1=Y(I-1)+(A-X(I-1))*(Y(I)-Y(I-1))/(X(I)-X(I-1))
C FUN1=Y(I-1)+(A-X(I-1))*(Y(I)-Y(I-1))/(X(I)-X(I-1))
C RETURN
C END
C*****************************************************************************
C SUBROUTINE CONTR1
C DIMENSION Y(10000),E(10000),D(10000),M(10000),L(10000)
C COMMON/CINT/H
C YSP=1.0
C AKC=1.0
C TAU1=1.0
C TAUD=1.0
C DO 3 I=1,10
C HSP-H(I-1)=E(I)
C D(I)=D(I-1)-AKC*E(I)+(DELT/TAU1)*E(I)
C +((TAUD*DELT)*(E(I)-E(I-1)+E(I-2)))
IF(D(I).LT.0.) THEN
  D(I)=0.
IF(D(I).GT.100.) THEN
  D(I)=100.
END
3 CONTINUE
END

******************************************************************************************