United States
Environmental Protection
Agency

Air Pollution Training Institute (APTI)
MD 17
Environmental Research Center
Research Triangle Park, NC

September 20

Control of Nitrogen Oxides Emissions

Student Manual

APTI Course 418

Author

John R. Richards, Ph.D., P.E.
Air Control Techniques, P.C.

Editor

Robert M. Schell
ICES Ltd.

Control of Nitrogen Oxides Emissions

Student Manual

APTI Course 418

Author

John R. Richards, Ph.D., P.E.
Air Control Techniques, P.C.

Editor

Robert M. Schell
ICES Ltd.

Developed by

ICES Ltd.
September 2000
EPA Contract No. 68D99022

Acknowledgments

This text combines original content provided by Dr. John R. Richards, Ph.D., P.E., with the content of EPA Workshop T002-99, *Control of Nitrogen Oxides Emissions*, which was broadcast in January 1999 to the APTI Distance Learning Network. The author of this student manual, Dr. Richards, and the editor, Robert M. Schell, are hereby acknowledged for their cooperative integration of the original broadcast materials with extended and updated technical content. The T002-99 Workshop presenters who currently appear in the broadcast video are also acknowledged for the original content they contributed. These materials provided a firm foundation and a companion video for this course. The presenters and the chapters of this manual that contain their contributions are given here.

	Chapter 1	Introduction to Nitrogen Oxides Control
	Mike Urban	
Chapter 2	NO_X Formation in Combustion Processes	Bob Hall
	Chapter 3	NO_X Emission Trends and Sources
	Douglas Soloman	
Chapter 4	NO_X Regulatory Programs	Dave Stonefield, Ravi Srivastava
Chapter 5	Combustion Sources	John R. Richards
Chapter 6	Combustion Modifications	Andy Miller
Chapter 7	Low NO_X Burners	Andy Miller
Chapter 8	NO_X Reburning	Bob Hall
Chapter 9	Reciprocating Internal Combustion Engines	Jack Wasser
Chapter 10	Gas Turbines	Sims Roy
Chapter 11	Selective Catalytic Reduction	Anne Johnson
	Chapter 12	Selective Non-Catalytic Reduction
	John R. Richards	
Chapter 13	Continuous Emission Monitoring	James A. Jahnke

Disclaimer

This document is not an official policy and standards document and does not constitute U.S. Environmental Protection Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Classroom Agenda

Course 418
Control of NO_X Emissions

DAY 1

Introduction and Organization of the Course

Pre-test

Chapter

1 Introduction to Nitrogen Oxides Control
Regulation of NO_X
Definition of NO_X
Origins of NO_X

2 NO_X Formation in Combustion Processes
Introduction
NO_X formation mechanisms in combustion processes

3 NO_X Emission Trends and Sources
Anthropogenic sources
Natural sources
NO_X emission trends
Ozone season emissions
Emissions projections

4 NO_X Regulatory Programs
Introduction
NO_2 NAAQS
Ozone NAAQS
PM_{10} and $PM_{2.5}$ NAAQS
Visibility impairment
Historic review of ozone control strategies
Acid rain
Other programs

5 Combustion Sources
Boilers
Stationary internal combustion engines
Municipal waste incinerators

Classroom Agenda

Course 418

Control of NO_X Emissions

DAY 2

Chapter

6 Combustion Modifications

Principles of combustion modifications
Combustion modification techniques
Summary

7 Low NO_X Burners

LNB operating principles
Wall-fired LNBs
Tangentially-fired LNBs
Operational issues

8 NO_X Reburning

Introduction
Reburning operating principles
Wall-fired reburning
Cyclone boiler reburning
Video Segment
Applicability

9 Reciprocating Internal Combustion Engines

Pre-combustion control
Post-combustion control
Case study

10 Gas Turbines

Introduction
Combustion modification controls
Post combustion controls

Classroom Agenda

Course 418

Control of NO_X Emissions

DAY 3

Chapter

11 Selective Catalytic Reduction

- Introduction
- Operating principles
- SCR configuration
  - **Video Segment**
- Reagent (ammonia) injection system
- Catalyst
  - **Video Segment**
    - Instrumentation

12 Selective Non-Catalytic Reduction

- Development
- Operating principles
- System components
- Design and sizing
- Operation
  - **Video Segment**

13 Continuous Emission Monitoring

- CEM regulatory program
- Measurement techniques
- CEM systems
- Quality assurance and quality control
- Oxygen concentration monitors
- Emissions calculations

Post-test

Adjourn

TABLE OF CONTENTS

ACRONYMS

ACRONYMS	**Definitions**
ACFM	Actual cubic feet per minute
AEL	Alternative emission limit
AIRS	Aerometric Information Retrieval System
BACT	Best available control technology
BBF	Burner biased firing
BDC	Bottom dead center
BEISE-2	Biogenic Emissions Inventory System-2
BOOS	Burners out of service
Btu's	British thermal units
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAM	Compliance Assurance Monitoring
CCOFA	Close coupled overfire air
CCT	Clean coal technology
CEM	Continuous emission monitoring
CFB	Circulating fluid beds
CFD	Computational fluid dynamic
CGA	Cylinder gas audit
CGSU	Centimeter gram second units
COFA	Closed overfire air
DAS	Data acquisition system
DOD	Department of Defense
DLN	Dry low NO_X
DOE	Department of Energy
DSCFM	Dry standard cubic feet per minute
EAA	Electric aerosol analyzer
EDS	Energy dispersive X-ray spectroscopy
EGR	Exhaust gas recirculation
EGU	Electric generating units
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic precipitator
FBC	Fluid bed combustors
FEGT	Furnace exit gas temperature
FETC	Federal Energy Technology Center
FGC	Flue gas conditioning
FGR	Flue gas recirculation
FHA	Federal Highway Administration
FIP	Federal Implementation Plan
fpm	Feet per minute
FRP	Fiberglass reinforced plastics

GFC	Gas filter correlation
GCVTC	Grand Canyon Visibility Transport Commission
HAP	Hazardous Air Pollutant
HPMS	Highway Performance Monitoring System
HRSG	Heat recovery steam generator
IC	Internal combustion
ID Fan	Induced draft fan
INFR	In-furnace Reduction
IR	Infrared
KW	Kilowatt
kWh	Kilowatt hour
LAER	Lowest achievable emission rate
LEA	Low excess air
LEL	Lower explosive limit
LNB	Low-NO_X burners
LOI	Lost on ignition
MACT	Maximum achievable control technology
MC	Medium cure
MMD	Mass median diameter
MND	Median number diameter
MNL(s)	Multiple nozzle lances
MVD	Median volume diameter
MW	Megawatt
MWe	Megawatts of electrical power
MWh	Megawatt-hour
NAAQS	National Ambient Air Quality Standards
NAPAP	National Acid Precipitation Assessment Program
NDIR	Nondispersive infrared
NDUV	Nondispersive ultraviolet
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NET	National Emission Trends Inventory
NIST	National Institute of Standards and Technology
NOTR	Northeast Ozone Transport Region
NO_X	Nitrogen Oxides
NSPS	New Source Performance Standards
NSR	New Source Review
OFA	Over fire air
OMS	Office of Mobile Sources
OTAG	Ozone Transport and Assessment Group
OTC	Ozone Transport Commission
PEMS	Predictive emission monitoring systems
PLM	Polarizing light microscopy
ppm	Parts per million
PSD	Prevention of significant deterioration

PSI	Pounds per square inch
PSIG	Pounds per square inch gauge
PTFE	Polytetrafluoroethylene
PURPA	Public Utilities Regulatory Policies Act
R&D	Research and development
RA	Relative accuracy
RAA	Relative accuracy audit
RACT	Reasonably available control technology
RATA	Relative accuracy test audit
RC	Rapid cure
RM	Reference method
RPM	Revolutions per minute
SARA	Superfund Amendments and Reauthorization Act
SC	Slow cure
SCA	Specific collection area
SCAQMD	South Coast Air Quality Management District
SCFM	Standard cubic feet per minute
SCR	Selective catalytic reduction
SEM	Scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
SI	Spark ignition
SIP(s)	State Implementation Plan(s)
SMD	Sauter mean diameter
SNCR	Selective non-catalytic reduction
SOFA	Separated over fire air
SR	Stoichiometric ratio
SRM	Standard Reference Materials
SS	Slow setting
STP	Standard temperature and pressure
TDC	Top dead center
T-R	Transformer rectifier
TSP	Total suspended particle
UBC	Unburned carbon
ULNB	Ultra low-NO_X burners
UV	Ultraviolet light
VMT	Vehicle miles traveled
VOCs	Volatile organic compounds
W.C.	Water column

LIST OF TABLES

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 6

CHAPTER 8

CHAPTER 9

CHAPTER 10

CHAPTER 13

LIST OF FIGURES

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

CHAPTER 9

CHAPTER 10

CHAPTER 11

CHAPTER 12

CHAPTER 13

FORWARD

This student manual is intended to be used either in conjunction with EPA's Broadcast Video T-002 or in the classroom as a supplement to the instructor's materials.

This manual is organized into 13 chapters that examine the environmental importance of NO_X, how it is formed, its sources, its regulation and control.

- Chapter 1, *Introduction,* introduces NO_X and significant related compounds.
- Chapter 2, *Formation of* NO_X*,* describes the mechanisms of NO_X formation during the combustion process and the secondary pollutants formed as a result of atmospheric reactions.
- NO_X emission source categories, emission trends, and major stationary combustion sources are described in Chapter 3, NO_X *Emissions Trends and Sources*.
- Chapter 4, *Regulations,* presents a discussion of NO_X–related emissions regulations, which increasingly focuses on stationary source emitters.
- Chapter 5, *Combustion Sources,* examines the nature of stationary combustion sources as NO_X emitters.
- Chapters 6, 7, and 8 (*Combustion Modifications, Low* NO_X *Burners,* and NO_X *Reburning*, respectively) discuss pre-combustion NO_X control techniques currently applied to stationary sources.
- Chapter 9, *Reciprocating Internal Combustion Engines*, discusses internal combustion engines as a brief introduction to mobile sources, in itself a complex and expansive topic.
- Gas turbines are discussed in Chapter 10.
- Add-on control systems are discussed in Chapter 11, *SCR Systems*, and Chapter 12, *SNCR Systems*.
- Chapter 13, *Continuous Emission Monitoring*, presents the basic concepts of continuous emission monitoring of NO_X emissions, which is required of many facilities.

The manual is organized according to the instructor presentations that are included in EPA's Broadcast Video T-002 and contains all the materials and information that are presented by each instructor. *Additional information* that is relevant to the topics being discussed, but not presented in the video, is also included in this manual. ***This supplemental information is clearly denoted in the manual by a bold vertical line along its left and right margins.***

BIBLIOGRAPHY OF TECHNICAL ARTICLES AND MANUALS

GENERAL

Acurex Environmental. *Evaluation and Costing of NO_X Controls for Existing Utility Boilers in the NESCAUM Region.* Report (Draft) prepared for U.S. EPA, RTP, NC. September 1991.

Acurex Environmental. *Phase II NO_X Controls for The MARAMA and NESCAUM Regions.* Prepared for U.S. EPA, Office of Air Quality Planning and Standards. September 1995.

Antos, R. *Emission Control Techniques for Westinghouse Industrial Combustion Turbines.* Paper 92-136.07. Presented at the 85th Annual Meeting & Exhibition of the Air & Waste Management Association, Kansas City, MO. June 21-26, 1992.

Arai M. et al. *External EGR Effect on Spray Combustion. Environmental Control Fuels and Combustion Technologies.* American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 389-397. 1997.

Babcock & Wilcox Company, Inc. *Steam, Its Generations and Use.* Barberton, OH. 1972.

Baldwin, A. et al. *Role of the U.S. Clean Coal Technology Program in Implementing the Objectives of the Joint Canada-U.S. Acid Rain Mitigation Initiative.* Proceedings of the Air and Waste Management Association's Annual Meeting and Exhibition, Paper 97-TP58.05, Pittsburgh, PA. 1997.

Battye, R., W. Battye, C. Overcash, and S. Fudge. *Development and Selection of Ammonia Emission Factors.* Atmospheric Research and Exposure Assessment Laboratory, EPA, Research Triangle Park, NC. August 1994.

Bertacchi S. et al. *ORIMULSION™ Firing in Low-NO_X Combustion Systems. Environmental Control Fuels and Combustion Technologies.* American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 623-632, American Society of Mechanical Engineering, Fairfield, NJ. 1997.

Boyle R. et al. *Simultaneous Reduction of NO_X and Heat Rate at TVA's Johnsonville Steam Plant Using Sequential Process Optimization.* Proceedings of the 1995 International Joint Power Generation Conference, Environmental Control Fuels and Combustion Technologies, American Society of Mechanical Engineering, Environmental Control Division Publication, Volume 1, Pages 37-45, New York, NY. 1995.

Bretz, E. *Lower Limits on Engine Emissions Force Post-Combustion Treatment.* Power, Pages 65-68. May 1989.

Buffa, T. and D. Marti, United Illuminating and R. Laflesh. *Award-Winning NO_X Control at Bridgeport Harbor.* Power Engineering, Pages 51-55. December 1995.

Chang, M. and C. Cheng. *Plasma-Assisted Removal of NO from Gas Streams via Ammonia Injection.* Environmental-Engineering Science, Volume 14, Number 4, Pages 193-200. 1997.

Chatttopadhyay, P. *Boiler Operations, Questions and Answers.* McGraw Hill, Inc., New York, NY. 1994.

Chen, J. et al. *Commercial Development of Oxidation Catalyst for Gas Turbine Cogeneration Applications.* Presented at the 82nd Annual Meeting of the Air and Waste Management Association, Anaheim, CA. June 1989.

Colannino, J. John Zink. *Using Modified Response Surface Methodology (MRSM) to Control NOx.* Paper presented at the Industrial Clean Air Companies Forum, Durham, NC. March, 1998.

Cuenca, M.A., and E.J. Anthony. *Pressurized Fluidized Bed Combustion.* Blackie Academic & Professional, New York, NY. 1995.

Davis, L. *Dry Low NO_X Combustion for General Electric Heavy Duty Gas Turbines.* Paper 89-75, 4. Presented at the 82nd Annual Meeting & Exhibition of the Air and Waste Management Association, Anaheim, CA. June 25-30, 1989.

Dirk J. *Pre and/or Post Environmental Permitting for Emerging Technologies and Their Emission Controls.* Environmental Control Fuels and Combustion Technologies. American Society of Mechanical Engineers, Environmental Control Division Publication, Volume 5, Pages 93-96, American Society of Mechanical Engineering. 1997.

Donovan D. et al. *School of (Hard) NO_X:* The Ozone Transport Commission NOx Budget Program. New England Power Co., Proceedings of the Air and Waste Management Association's Annual Meeting and Exhibition, Paper 97-WP80B.03, Pittsburgh, PA. 1997.

Eskinazi, D. *Retrofit NO_X Control Strategies for Coal-Fired Utility Boilers.* Report No. 91-94.5. Presented at the 84th Annual Meeting & Exhibition of the Air & Waste Management Association. Vancouver. June 1991.

Estrada J. et al. *Management of Southern California Edison's NO_X Reduction Program in a Changing Regulatory Environment.* Proceedings of the 1995 International Joint Power Generation Conference, Environmental Control Fuels and Combustion Technologies, American Society of Mechanical Engineers Environmental Control Division Publication, Volume 1, Pages 47-59. 1995.

Frazier W. et al. *Regulatory and Technical Options for Cost-Effective NO_X Control for Power Producers.* Environmental Control Fuels and Combustion Technologies Nuclear Engineering American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 37-44. 1997.

Frazier W. et al. *Coordinate NOx Control Strategies: Phase II Title IV, Ozone Transport Region and Ozone Transport Assessment Group.* Proceedings of the American Power Conference, Volume 1, Pages 533-540, 1998.

Fujii S. et al. *Hybrid Combustion Control System for Refuse Incineration Plant.* NKK Technical Review, Number 78, Pages 25-30. July 1998.

Gartner, E. and C. Wilk. *Nitrogen Oxide Emissions from Raw Materials in Cement Kilns.* Paper 84-44.8. Presented at the 77th annual Meeting of the Air Pollution Control Association, San Francisco, CA. June 24-29, 1984.

Hansen, E. *The Use of Carbon Monoxide and Other Gases for Process Control.* IEEE Transactions of Industry Applications, Volume. IA-22, Number. 2. March/April 1986.

Hasegawa T. et al. *High Temperature Air Combustion Contributing to Energy Saving and Pollutant Reduction in Industrial Furnace.* Environmental Control Fuels and Combustion Technologies. American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 259-266. 1997.

Helfritch D., S.Bortz, and P. Bergman. *Integrated Dry Sorbent Injection for Coal-Fired Boiler SO_2 and NO_X Control.* Paper No. 90-103.4. Presented at the 83rd Annual Meeting and Exhibition of the Air and Waste Management Association, Pittsburgh, PA. June 1990.

Hofmann, J., B. Luftglass,. W. Sun, J Quitno, and R.Pachaly. *NO_X Control for Municipal Solid Waste Combustors.* Paper 90-25.2. Presented at the 83rd Annual Meeting & Exhibition of the Air & Waste Management Association, Pittsburgh, PA. June 24-29, 1990.

Hull, R. et al. *NO_X Control Technology Data Base for Gas-Fueled Prime Movers.* Phase I. Report prepared by Southwest Research Institute for Gas Research Institute. April 1988.

Hunter, S. and R. Benson. *Reduction of Nitric Oxide Emissions on a Full-Scale Cement Kiln Using Primary Air Vitiation.* In Proceedings of 1985 Symposium on Stationary Combustion NO_X Control. Electric Power Research Institute Report CS-4360, Volume 2. January 1986.

Keating, E.L. *Applied Combustion.* Marcel Dekker, Inc. New York, NY. 1993.

LaRue, A and P. Cioffi. *NO_X Control Update*. Presented at the Joint Symposium on Stationary Combustion NO_X Control, San Francisco, CA, March 1989.

Lazzeri L. and R. DeSantis. *Further Experience for Environmental Improvement in Fossil Fuel Combustion.* Proceedings of the American Power Conference, Volume 1, Pages 187-195. Chicago, IL. 1998.

Makansi, J. *Focus of NO_X Removal Shifts From Process Design to Optimization.* Power, Pages 47-49. January 1980.

Makansi, J. *Reducing NO_X Emissions from Today's Power Plants.* Special Report. Power Engineering, Pages 11-28. May 1993.

Makansi, J. *SO_X/NO_X Control, Fine Tuning for Phase 1 Compliance.* Power, Pages 15-26. March 1994.

Malte P. and K. Nichols. *Evaluation of NO_X Production from Black Liquor Gasification-Gas Turbine Combustion Systems.* International Chemical Recovery Conference, Volume 2, Pages 705-720, TAPPI Press, Norcross, GA. 1998.

McElroy, M, J. Maulbetsch, and D. Eskinazi. *Retrofit NO_X Control Options for Coal-Fired Electric Utility Power Plants.* Journal of the Air Pollution Control Association. Volume 36, Page 1924. 1986

McGavin, C. et al. *FBC Testing of Coal/RDF Mixtures.* Presented at the 10th International Conference on Fluidized Bed Combustion, San Francisco, CA. May 1989.

Midwest Research Institute. *Alternative Control Techniques Document – Stationary Combustion Gas Turbines.* Draft. Report Prepared for the U.S. EPA, Research Triangle Park, N.C. July 1991.

Muller P. *Effectiveness Analysis of Implementing the Regional Clean Air Incentives Market (RECLAIM) Program to Reduce Emissions in the South Coast Air Basin. South Coast Air Quality Management District.* Proceedings of the Air and Waste Management Association's Annual Meeting and Exhibition, Paper 97-WA80A.02, Pittsburgh, PA. 1997.

Power. *Natural Gas as a Power Plant Fuel.* Special Report. Power, Pages 35-42. February 1994

Nichols, K., L. Thompson and J. Empie. *A Review of* NO_X *Formation Mechanisms in Recovery Furnaces.* TAPPI Journal, Volume 76, Number 1, Pages 119-124. January 1993.

Noble T. and D. Mayhew. *Keys to Successful Power Boiler Predictive Emissions Monitoring System Installation.* TAPPI Journal, Volume 2, Pages 593-597. 1997.

Nutcher, P.and D. Lewandowski. *Maximum Achievable Control Technology (MACT) for* NO_X *Emissions from VOC Thermal Oxidation.* Paper 94-WA74A.03. Presented at the 87th Annual Meeting and Exhibition of the Air and Waste Management Association, Cincinnati, OH. June 1994.

Pasini, S. et al. *Experimental Characterization of Flows in the Model of Strongly Swirling Combustor.* Proceedings of the Intersociety Energy Conversion Engineering Conference, Volume 2, Pages 916-920. 1997.

Patterson, P. PowerMAX, Inc. and M. Krieger. *Optimization Saves Money, Reduces* NO_X*.* Power Engineering, Pages 21-24. September 1997.

Penkala S. *Predicting Extreme Occurrences Using CEMS DATA.* Proceedings of the Air and Waste Management Association's Annual Meeting and Exhibition, Paper 97-RP145.03 Pittsburgh, PA. 1997.

Price, D. and S. Mandel. *Continuous Emission Monitor Post-Repair Decision Matrix for Quality Assurance Procedures.* Ultramar Inc, Annual ISA Analysis Division Symposium Proceedings, Volume 31, Pages 199-209. 1998.

Ruether J. et al. *Plant Betterment for an Anthracite-Burning Utility in Ukraine, Coal Preparation as Part of a* SO_2, NO_X *and Particulate Emission Control Strategy.* Proceedings of the Air & Waste Management Association's Annual Meeting and Exhibition, Paper 97-TA30A.04,. Pittsburgh, PA. 1997.

Sanders N. *Environmental Friendly Stainless Steel Pickling.* Solvay Inertox Research and Development, Anti-Corrosion Methods and Materials, Volume 44, Number 1, Pages 20-25. Jan--Feb, 1997.

Sanyal, A. et al. *Cost Effective Technologies for* SO_2 *and* NO_X *Control.* PowerGen Conference,, Volume 3, Page 71, Orlando, FL. November 17-19, 1992.

Schorr, M. *NO_X Emission Control for Gas Turbines: A 1992 Update on Regulations and Technology.* Paper No. 92-136.01. Presented at the 85th Annual Meeting & Exhibition of the Air & Waste Management Association, Kansas City, MO. June 21-26, 1992.

Seidman, N. *Stationary Source Nitrogen Oxides Control Strategies in the Northeastern States.* Paper 91-94.6, Presented at the 84th Annual Meeting & Exhibition of the Air & Waste Management Association. Vancouver, BC. June, 16-21, 1991.

Sidebotham, G., and R. Williams. *Technology of NO_X Control for Stationary Gas Turbines.* Center for Environmental Studies, Princeton University. January 1989.

Singer, J., Editor. *Combustion, Fossil Power Systems.* Combustion Engineering, Inc. Windsor, CT. 1981.

TRW, Inc. *Emissions Assessment of Conventional Stationary Combustion Systems.* Volume IV: Commercial/Institutional Combustion Sources. Publication No. EPA-600/7-71-003c. Prepared for the U.S. EPA. January 1981.

U.S. EPA. Field Tests of Industrial Stoker Coal-Fired boilers for Emission Control and Efficiency Improvement-Site E. EPA Publication No. EPA-600/7-80-064a. March 1980.

U.S. EPA. Field Tests of Industrial Stoker Coal-Fired boilers for Emission Control and Efficiency Improvement-Site H. EPA Publication No. EPA-600/7-80-112a. March 1980.

U.S. EPA. Emissions Assessment of Conventional Stationary Combustion Systems, Volume V: Industrial Combustion Sources. Publication No. EPA-600/7-81-003c. 1981.

U.S. EPA. NO_X Emission Factors for Wood-Fired Boilers. EPA Publication No. EPA-600/7-79-219. September 1979.

U.S. EPA Alternative Control Techniques Document-NO_X Emissions from Stationary Gas Turbines. EPA Publication EPA-453/R-93-007. January 1993.

U.S. EPA. Office of Air Quality Planning and Standards. National Air Quality and Emission Trends Report. 1997. Research Triangle Park, NC. EPA 454/R-98-016. December 1998.

U.S. EPA. Office of Air Quality Planning and Standards. Compilation of Air Pollutant Emission Factors (AP-42) – Section 8.8. 5th Edition. Research Triangle Park, NC February 1998.

U.S. EPA. Office of Air and Radiation. *Nitrogen Oxides: Impacts on Public Health and the Environment.* Research Triangle Park, NC. August 1997.

U.S. EPA. Overview of the Regulatory Baseline, Technical Basis, and Alternative Control Levels for Nitrogen Oxides Emission Standards for Small Steam Generating Units. Publication No. EPA-450/3-89-13, Office for Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC. May 1989.

U.S. EPA. Alternative Control Techniques Document-NO_X Emissions from Industrial/Commercial/Institutional (ICI) Boilers. EPA Publication EPA-453/R-94-022. March 1994.

U.S. EPA. Alternative Control Techniques Document-NO_X Emissions from Cement Manufacturing. EPA Publication EPA-453/R-94-004. March 1994.

U.S. EPA. Alternative Control Techniques Document-NOx Emissions from Process Heaters (Revised). EPA Publication EPA-453/R-93-034. September 1993.

U.S. EPA Alternative Control Techniques Document-NO_X Emissions from Iron and Steel Mills. EPA Publication EPA-453/R-94-065. September 1994.

U.S. EPA Alternative Control Techniques Document-NO_X Emissions from Utility Boilers. EPA Publication EPA-453/R-94-023. March 1994.

U.S. EPA. Integrated Air Pollution Control System. EPA Publication EPA 600/7-90-022b. 1990.

REBURNING

Adams B. and N. Harding. *Reburning Using Biomass For NO_X Control.* Fuel Processing Technology, Volume 54, Number 1-3, Pages 249-263. March 1998.

Schimmoller, B. *Orimulsion Rivals Gas as Reburn Fuel.* Power Engineering, Pages 32-36. February 1998.

Takeya R. and T. Nakamura. *Numerical and Experimental Investigation on the Application of Natural Gas Reburning to Municipal Solid Waste Incinerators.* Environmental Control Fuels and Combustion Technologies. American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 389-397. 1997

COMBUSTION MODIFICATIONS AND LOW NO_X BURNERS

Allen J. and P. Beal. *TAS Concept in Low NO_X Burner Designs.* Environmental Control of Fuels and Combustion Technologies. American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 195-199. 1997.

Dyr B. and J. Worley. *St. Johns River Power Park. Lowering NO_X Through Combustion Modification.* St. Johns River Power Park, Environmental Control Fuels and Combustion Technologies. American Society of Mechanical Engineers, Environmental Control Division publication, Volume 5, Pages 213-218. 1997.

Gollahalli S. *Emission Control From Cascade Burners.* American Society of Mechanical Engineers Environmental Control Division Publication, Volume 1, Pages 325-331. 1996.

John Zink. *Progress Continues in Gas-Turbine NO_X Control.* Power Engineering, Pages.19-21. May 1996.

Jones, C. *Maladies of New-NO_X Firing Come Home to Roost.* Power, Pages 54-60. January-February 1997.

Lauber, J., B. Cohen and R. Donais. *The Integration of Low NOx Technologies at the Southern Energy, Inc.* Birchwood Power Facility. Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium. August, 1997.

Radian Corporation. *Combustion Modification: NO_X Controls for Wall Fired and Tangentially Fired Boilers.* Prepared for U.S.EPA, Acid Rain Division.. July 1991.

U.S. EPA. *Emissions from Refinery Process Heaters Equipped with Low-NO_X Burners.* U.S. EPA Publication EPA-600/7-81-169. 1981.

Schorr, M. *NO_X Control for Gas Turbines: Regulations and Technology.* Paper presented at the Council of Industrial Boiler Owners NO_X Control IV Conference, Concord, CA. February 11-12, 1991.

Teng, H. *Combustion Modifications of Batch Annealing Furnaces and Ammonia Combustion Ovens for NO_X Abatement in Steel Plants.* Journal of the Air and Waste Management Association. Volume 46, Pages 1171-1178. December 1996.

U.S. EPA *Cost-Effectiveness of Low- NO_X Burner Technology Applied to Phase I, Group I Boilers.* Prepared for U.S. Environmental Protection Agency (contract No. 68 D3-0005). May 1995.

U.S. EPA. *Industrial Boiler Combustion Modification NO_X Controls.* Volume I: Environmental Assessment. EPA Publication No. EPA-600/7-81-126a. July 1981.

U.S. EPA. *Technology Assessment Report for Industrial Boiler Applications: NO_X Combustion Modification.* EPA Publication No. EPA-600/7-79-178f. December 1979.

Waibel, R. *Advanced Burner Technology for Stringent NO_X Regulations.* Presented at American Petroleum Institute Midyear Refining Meeting. May 8, 1990.

Washam, R. *Dry Low NO_X Combustion System for Utility Gas Turbine.* American Society of Mechanical Engineering Paper 83-JPGC-GT-13. September 1983.

SELECTIVE CATALYTIC REDUCTION

Baldwin, A. et al. *Is Selective Catalytic Reduction (SCR) an Attractive Option for NO_X Control in Coal-fired Power Plants?* Air & Waste Management Association Conference, Tempe, AZ. January 1995.

Cho S. *Properly Apply Selective Catalytic Reduction for NO_X Removal.* Chemical Engineering Progress, Pages 39-45. January 1994.

Cochran, J. et al. *Selective Catalytic Reduction for a 460 MW Coal Fueled Unit: Overview of a NO_X Reduction System Selection.* Presented at the 1993 Joint Symposium on Stationary Combustion NO_X Control, Bar Harbour, FL. May 24-27, 1993.

Cohen, Mitchell B. *Update on the Control of NO_X Emissions at the Southern Energy Inc. Birchwood Power Facility.* Paper presented at the Industrial Clean Air Companies Forum, Durham, NC. March, 1998.

Comprehensive Report to Congress, Clean Coal Technology, Demonstration of Selective Catalytic Reduction (SCR) Technology for the Control of Nitrogen Oxide (NO_X) Emissions from High-Sulfur, Coal-Fired Boilers. Southern Company Services Inc., DOE. April 1990.

Conway V. et al. *Case Study of Selective Catalytic Reduction System Start-Up on Digester Gas-Fired Combustion Turbines.* Paper 97-WP99.03, Proceedings of the Air and Waste Management Association's Annual Meeting and Exhibition, Pittsburgh, PA. 1997.

Emmel, T. et al. *Comparison of West German and U.S. Flue Gas Desulfurization and Selective Catalytic Reduction Costs.* U.S. Environmental

Protection Agency, Air and Energy Engineering Research Laboratory, EPA-publication 600/7-90-009. 1990.

Electric Power Research Institute. *Technical Feasibility and Cost of Selective Catalytic Reduction (SCR) NO_X Control.* EPRI Publication GS-7266, Palo Alto, CA. May 1991.

Healy, E. et al. *Economic Evaluation of Commercial-Scale SCR Applications for Utility Boilers.* Southern Company Services. September 1996.

Hinton, W. et al. Demonstration of Selective Catalytic Reduction (SCR) Technology for the Control of Nitrogen Oxides (NO_X) Emissions from High-Sulfur Coal-Fired Utility boilers at Plant Crist SCR Test Facility. Fourth Annual Clean Coal Technology Conference, Denver, CO. September 1995.

Hinton, W. et al. Demonstration of SCR Technology for the Control of NO_X Emissions from High-Sulfur Coal-Fired Utility Boilers. Fifth Annual Clean Coal Technology Conference, Tampa, FL. January 1997.

Institute of Clean Air Companies (ICAC), SCR Committee. *Selective Catalytic Reduction (SCR) for Controlling NO_X Emissions.* October 1994.

Jaerschky, et al. *SO_3 Generation-Jeopardizing Catalyst Operation?* Presented at the 1991 EPRI/EPA NO_X Control Symposium. March 1991.

Lauber, J., B. Cohen and R. Donais. *The Integration of Low NO_X Technologies at the Southern Energy, Inc. Birchwood Power Facility.* Presented at the EPRI-DOE-EPA Combined Utility Air Pollution Control Symposium. August, 1997.

Lowe, P, W. Ellison and M. Perlsweig. *Understanding the German and Japanese Coal-fired SCR Experience.* Presented at the 1991 Joint Symposium on Stationary Combustion NO_X Control. U.S. EPA/EPRI. March 1991.

Maxwell J. and Baldwin A. Demonstration of Selective Catalytic Reduction (SCR) Technology for the Control of Nitrogen Oxide (NO_X) Emissions form High-Sulfur, Coal-Fired Boilers. First Annual Clean Coal Technology Conference, Cleveland, OH. September 1992.

Perrin Quarles Associates. Draft Report, Performance of Selective Catalytic Reduction Technology at Electric Utility Boilers in the United States, Germany and Sweden. Report sponsored by the EPA Office of Air and Radiation, Acid Rain Program. October 1996.

Prosl, T. et al. *Technical Arguments and Economic Impact of SCR's Use for NO_X Reduction of Combustion Turbine for Cogeneration.* Paper presented at EPA Region 6 Meeting Concerning NOx Abatement of Combustion Turbines. December 17, 1987.

Radian Corporation. Plant Crist Environmental Monitoring Program. September 1996.

Rogers, W. and M. Durilla. *High Temp SCR Competes with DLN Combustors.* Power, Pages 55-56. March 1996.

Shareef, G. et al. and K. Locke. *Selective Catalytic Reduction NO_X Control for Small Natural Gas-Fired Prime Movers.* Paper No. 92-136.06. Presented at the 85th Annual Meeting and Exhibition of the Air and Waste Management Association, Kansas City, MO. June 1992.

Shareef, G. and D. Stone. *Evaluation of SCR NO_X Controls for Small Natural Gas-Fueled Prime Movers.* Phase I. Report Prepared by Radian Corporation for the Gas Research Institute. July 1990.

Southern Company Services, Inc. Final Report, Demonstration of Selective Catalytic Reduction (SCR) Technology for the Control of Nitrogen Oxide (NO_X) Emissions from High-Sulfur Coal-Fired Boilers, October 1996.

Urbas, J. and J. Boyle. *Design and Optimization of SNCR/SCR Hybrid on a Group1 Boiler in the Ozone Transport Region.* Presented at the PowerGen Conference, Orlando, FL. December 1998.

Verkamp et al. *Evaluation of SCR as a NO_X Control Option for Pacific Gas & Electric.* Paper presented at the 1993 EPRI/EPA NOx Control Symposium. May 1993.

Wagener, P and G. Cook, U.S. Generating Co. *SCR Succeeds at Logan Generating Plant.* Power Engineering, pp.28-32. January 1997.

SELECTIVE NON-CATALYTIC REDUCTION

Institute of Clean Air Companies (ICAC) SNCR Committee. Selective Non-Catalytic Reduction (SNCR) for Controlling NO_X Emissions. July 1994.

Jones, D et al. *Two Stage DeNO$_X^®$ Process Test Data for 330 TPD MSW Incineration Plant.* Presented at the 82nd Air Pollution Control Association Annual Meeting and Exhibition. Anaheim, CA. June 1989.

Jones, D. et al. *Two-Stage DeNO$_X^®$ Process Test Data from Switzerland's Largest Incineration Plant.* EPRI/EPA Joint EPA/EPRI Symposium on Stationary Combustion NOx Control, San Francisco, CA. March 1989.

Lyon, R. *Thermal DeNO$_X^®$.* Environmental Science and Technology, Volume 21, Page 231. 1987.

Michael, M. et al. *Urea Injection NO_X Removal on a 325 MW Brown Coal-Fired Electric Utility Boiler in West Germany.* 52nd Annual Meeting American Power Conference, Chicago, IL. June 1989.

Mincy, J. *SNCR Technology: The Next Generation.* Presented at NO_X Conference, Long Beach, CA. February 10-11, 1992.

Moilanen, G. K. Price, C. Smith and A. Turchina. *Noncatalytic Ammonia Injection for NO_X Reduction on a Waste Wood Fired Boiler.* Paper No. 87-6.6. Presented at the 89th Annual Meeting of the Air Pollution Control Association. June 21-26, 1987.

Muzio, L et al. *Noncatalytic NO_X Removal with Ammonia.* Electric Power Research Institute FP-735. April 1978.

Muzio, L. and J. Arand. *Homogenous Gas Phase Decomposition of Oxides of Nitrogen.* Electric Power Research Institute FP-253. 1976.

Muzio, L. and T. Montgomery. *N_2O Formation in Selective Non-Catalytic NO_X Reduction Processes.* Paper presented at 1991 Joint Symposium on Stationary Combustion NOx Control, Washington, D.C. November 1991.

Pachaly, R., J. Hofmann, and W. Sun. *The NO_XOUT^C Process for the Control of the NO_X Emissions from Waste Incinerators.* Paper No. 91-34.6. Presented at the 84th Annual Meeting & Exhibition of the Air and Waste Management Association, Vancouver, British Columbia. June 16-21, 1991.

Quartucy, G., M. Mansour, and J. Nylander. *Full Scale Urea Injection Evaluation.* Paper No. 87-6.1. Presented at the 80th Annual Meeting of Air Pollution Control Association. June 21-26, 1987.

Rummenhohl, V. et al. *Relating the $DeNO_X$® Experience to U.S. Plants: Lessons from More Than 30,000 MW of $DeNO_X$® Retrofits.* Presented at the American Society of Mechanical Engineering Joint International Power Generation Conference, Phoenix, AZ. October 1994.

Teixeira, D. *Widening the Urea Temperature Window.* In Proceedings of the 1991 Joint EPA/EPRI Symposium on Stationary Combustion NO_X Control. 1991.

Zhou, Q. and S. Yao, A. Russell and J. Boyle, Dept of Mechanical engineering, Carnegie Mellon University, Pittsburgh, PA. *Flue Gas NO_X Reduction Using Ammonia Radical Injection.* Journal of the Air & Waste Management Association. Volume 42, No. 9, pages 1193-1198. September 1992.

Review Answers

Chapter 1 – Introduction to Nitrogen Oxides Control

1. a. Insoluble

2. e. 5%

3. a. NO_2 NAAQS
   b. Ozone NAAQS
   c. Acid Rain
   d. $PM_{2.5}$
   e. Regional Haze

4. b. NO_2
   c. HNO_3
   e. N_2O_4

Chapter 2 – Formation in Combustion Processes

1. a. High gas temperature
   b. High oxygen concentrations
   c. High residence time at high gas temperature

2. b. Zeldovich mechanism

3. d. 50% to 80%

4. a. 0.5% to 2%

5. c. Natural gas

Chapter 3 – NO_X Emission Trends and Sources

1. c. Remained relatively constant

2. b. Gasoline-powered lawn mower
   c. Diesel generator
   e. Front-end loader

3. c. Coal-fired boilers

4. c. 1977

5. c. 1978

Chapter 4 – NO_X Regulatory Programs

1. e. All of the above.

2. c. Emitted by numerous stationary and mobile sources.

3. a. iii
   b. ii
   c. i
   d. iv

4. a. i
   b. iii
   c. ii
   d. iv

5. c. 1970

6. d. 1990

7. a. Sulfur dioxide
   c. Nitrogen oxides

Chapter 5 – Combustion Sources

1. c. 600°F to 700°F

2. a. 300°F to 350°F

3. b. Lower

4. d. 20% to 50%

5. c. 5% to 25%

6. d. Cyclone-fired boiler

7. b. Tangentially-fired boiler

8. b. Peaking service
   c. Emergency service
   d. Gas compressor stations

9. a. Cogeneration unit

10. b. Four-stroke reciprocating CI engine

Chapter 6 – Combustion Modifications

1. a. Carbon monoxide formation
   b. Increased combustible levels in fly ash
   c. Boiler tube fouling

2. b. Increase

3. a. Fuel/air ratio set by the boiler controller
   b. Air infiltration into the boiler

4. c. Decreased boiler efficiency

5. c. Minimize the flame temperatures and oxygen concentrations by injecting combustion products into the burner flame zone.

6. c. Low excess air

7. a. Burners-out-of-service
   c. Biased burner firing

8. c. Reduced air preheat
   d. Flue gas recirculation

9. a. 25% to 30%

10. a. Nitrogen oxides

Chapter 7 – Low NO_X Burners

1. b. The primary zone is fuel rich
   c. Oxygen is limited in the primary zone

2. e. None of the above

3. a. Reducing the peak flame temperature
   c . Recirculating the flue gas

4. a. Mixing of the fuel and air in a slow controlled pattern
   b. High LOI levels
   d. Recirculation of combustion gases

5. c. 20% to 50 %

6. a. Staged fuel burner

7. b. Elongated flame
   c. Divided flame
   d. Swirling flame

8. a. Recirculation combustion products
   b. A localized reduction of available oxygen
   c. A reduction of the peak flame temperature
   d. Increased static pressure drop of the boiler

9. d. Creating a more distinct separation between the fuel-rich and air-rich zones.

10. b. Poor coal distribution in injection ports and tubes

Chapter 8 – NO_X Reburning

1. c. 50% to 70 %

2. a. sub-stoichiometric

3. a. off-stoichiometric combustion

b. staged fuel combustion

4. b. HCN
   c. hydrocarbon radicals

5. b. Results in a reduction of SO_2 emissions.
   d. It provides rapid burnout.

6. c. 0.9

7. d. Formation of fly ash on the walls and the rubes of the boiler.

8. a. Particulate matter
   b. Nitrogen dioxide
   c. Sulfur dioxide
   d. Carbon dioxide

9. a. Electric generating units
   b. Municipal waste incinerators

10. c. 0.3 seconds

Chapter 9 – Reciprocating Internal Combustion Engines

1. d. CI engines operate at higher pressures than SI engines.

2. a. $\phi < 1$

3. b. CO emissions will increase
   c. Hydrocarbons will increase

4. b. CI engines run slightly fuel-lean
   c. CI engines operate at higher pressures

5. a. Lead in the fuel
   d. Lubricating impurities

Chapter 10 – Gas Turbines

1. a. Natural gas is lower in sulfur content and other potentially damaging impurities.
   d. Natural gas burns at a lower temperature than fuel oils reducing thermal NO.

2. a. It is a cost-efficient NO_X control option.
   b. Can be applied in conjunction with post combustion control techniques.

3. b. The power output is increased.

4. c. Limiting the flame temperature.

5. e. None of the above

6. a. Provide better combustion stability.
   b. Reduces pressure oscillations.
   c. Increases the life span of turbine components.
   d. Reduces NO$_x$ emissions.

7. b. Mid 1980s

8. d. 30 ATM

9. a. 600°F to 800°F

10. b. SCR
    c. XONON™
    d. SCONOx™

Chapter 11 – Selective Catalytic Reduction

1. b. It may cause a secondary plume formation.
   c. It represents reagent loss.
   d. Fly ash contamination may occur.

2. d. Flue gas temperatures are lower than desired.

3. a. 50% to 90%

4. c. 3% to 5%

5. b. Tungsten trioxide

6. a. Plugging
   a. Blinding
   e. Masking

7. a. Startup
   b. Shutdown
   b. Periods of abnormally high flue gas temperatures

8. a. 70% to 90%

Solution:

$$\left(\frac{2.7\text{ lb moles NO}_x}{\text{hr}}\right)\left(\frac{1\text{ hr}}{60\text{ min}}\right)\left(\frac{0.90\text{ lb moles NH}_3}{1.0\text{ lb moles NO}_x}\right) = 0.41\text{ lb moles NH}_3\text{/min}$$

0.41 lb moles NH_3/min

Chapter 12 – Selective Non-Catalytic Reduction Systems

1. b. 1600°F to 1900°F

2. a. One mole of NH_3 per mole of NO_X

3. c. One-half mole of urea per mole of NO_X

4. b. Moles of NO_X reduced per mole of reagent injected

5. a. Gas temperatures on the low end of the optimum temperature range

6. d. All of the above

7. d. All of the above

8. e. All of the above

9. b. Ammonium chloride
   d. Nitrous oxide
   e. Carbon monoxide

10. a. Reagent costs are reduced by the decreased NO_x levels provided by combustion modifications and low NO_x burners.

Chapter 13 – Continuous Emission Monitoring

1. d. In-situ double-pass path system

2. a. Misalignment of optical components due to stack vibrations.
   d. Inaccessibility to filter

3. a. iii.
   b. ii.
   c. i.
   d. iii.

4. a. GFC

5. c. Monitor burner operation
   d. Determining air infiltration
   e. Limit thermal NO_X formation

6. *Solution (a):*

   Step 1. Determine the actual dry concentration of NO_x in the flue gas.

$$c = \frac{c_{wet}}{1 - B_{ws}} = \frac{120 \text{ ppm}_v}{1 - 0.09} = 132 \text{ ppm}_{vd} \text{ (actual)}$$

   Step 2. Correct to 12 % CO_2.

$$C_{@12\%CO_2} = C\left(\frac{12.0}{\%C\,O_2}\right) = 132\left(\frac{12.0}{8.0}\right) = 198 \text{ ppm}_{vd@12\%CO_2}$$

   Solution (b):

   Step 1. Determine the gas flow rate on a dry standard basis from Equation 13-12.

$$Q_{dscfh} = \left(20 \text{ ft}^2\right)(20 \text{ ft/sec})\left(\frac{3600 \text{ sec}}{\text{hr}}\right)(1 - 0.09)\left(\frac{528}{702}\right)\left(\frac{30.1}{29.92}\right) = 992{,}000 \text{ dscfh}$$

   Step 2. Determine the emissions rate from Equation 13-12.

$$\text{ER (lb NO}_x\text{/hr)} = (992{,}000 \text{ dscfh})\,132 \text{ ppm}\left(\frac{\text{lb NO}_x}{8.375 \times 10^6 \text{ scf}}\right) = 15.6 \text{ lb NO}_x\text{/hr}$$

FORWARD

This student manual is intended to be used either in conjunction with EPA's Broadcast Video T-002 or in the classroom as a supplement to the instructor's materials.

This manual is organized into 13 chapters that examine the environmental importance of NO_X, how it is formed, its sources, its regulation and control.

- Chapter 1, *Introduction,* introduces NO_X and significant related compounds.
- Chapter 2, *Formation of* NO_X*,* describes the mechanisms of NO_X formation during the combustion process and the secondary pollutants formed as a result of atmospheric reactions.
- NO_X emission source categories, emission trends, and major stationary combustion sources are described in Chapter 3, NO_X *Emissions Trends and Sources*.
- Chapter 4, *Regulations,* presents a discussion of NO_X–related emissions regulations, which increasingly focuses on stationary source emitters.
- Chapter 5, *Combustion Sources,* examines the nature of stationary combustion sources as NO_X emitters.
- Chapters 6, 7, and 8 (*Combustion Modifications, Low* NO_X *Burners,* and NO_X *Reburning*, respectively) discuss pre-combustion NO_X control techniques currently applied to stationary sources.
- Chapter 9, *Reciprocating Internal Combustion Engines*, discusses internal combustion engines as a brief introduction to mobile sources, in itself a complex and expansive topic.
- Gas turbines are discussed in Chapter 10.
- Add-on control systems are discussed in Chapter 11, *SCR Systems*, and Chapter 12, *SNCR Systems*.
- Chapter 13, *Continuous Emission Monitoring*, presents the basic concepts of continuous emission monitoring of NO_X emissions, which is required of many facilities.

The manual is organized according to the instructor presentations that are included in EPA's Broadcast Video T-002 and contains all the materials and information that are presented by each instructor. Additional information that is relevant to the topics being discussed, but not presented in the video, is also included in this manual. ***This supplemental information is clearly denoted in the manual by a bold vertical line along its left and right margins.***

1 Introduction to Nitrogen Oxides Control

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Name the five major issues that are currently driving the regulation of NO_X.
2. Discuss the relationship between nitric oxide and nitrogen dioxide in atmospheric reaction.
3. Name the primary health and environmental effects of NO_X.
4. Explain the relationship of NO_X to ozone.

1 Introduction to Nitrogen Oxides Control

1.1 REGULATION OF NITROGEN OXIDES

1.1.1 Historic Overview

The regulation of NO_X dates back to the State Implementation Plans (SIPs) that were developed in the early 1970s in response to the requirements contained in the Clean Air Act Amendments (CAAA) of 1970. The regulations contained within SIPs were initially designed to attain the National Ambient Air Quality Standard (NAAQS) for nitrogen dioxide.

The 1970 CAAA also required EPA to establish New Source Performance Standards (NSPS) that specify control requirements for new sources of any criteria pollutant, including NO_X. For example, the NSPS for utility boilers in 40 CFR Part 60, Subpart D, that was established in 1970 includes control requirements for NO_X.

More recently, because NO_X reacts in the atmosphere to form acid rain, EPA has imposed acid rain requirements on fossil fuel-fired utility boilers to achieve Phase I compliance in 1995 and Phase II compliance in the year 2000. These acid rain requirements impose limitations on NO_X emissions.

In summary, regulatory agencies have been regulating NO_X emissions for over 30 years. However, there is now a realization that there is a need for additional NO_X controls that go beyond current requirements. This realization is based on the role that NO_X plays in the formation of ozone and photochemical smog.

1.1.2 Ozone NAAQS, NO_X SIP Call and Section 126 Petitions

Although it has been recognized for about forty years that NO_X is one of the key reactants leading to the formation of ozone, the initial control efforts for attaining the ozone NAAQS focused on volatile organic compound (VOC) emissions. It is now recognized that additional NO_X control will be needed to meet the new ozone NAAQS that was promulgated in July 1997.

For the same reason, NO_X control will be essential to achieve ozone levels in the 22 States and the District of Columbia recently subject to the NO_X SIP Call.

NO_X SIP CALL

On October 27, 1998, EPA published a Federal Register notice that required 22 states and the District of Columbia to submit SIPs that address the regional transport of ground-level ozone by reducing emissions of NO_X. Figure 1-1 identifies the states and territories that were originally subject to the Call. After the issue of the NO_x Sip Call, several parties challenged EPA in court. On March 3, 2000, the United States Court of Appeals for the District of Columbia Circuit issued a decision to uphold the NO_x SIP Call in all states except Wisconsin, western Missouri and southern Georgia. The rule requires emission reduction measures to be in place by May 1, 2003.[1]

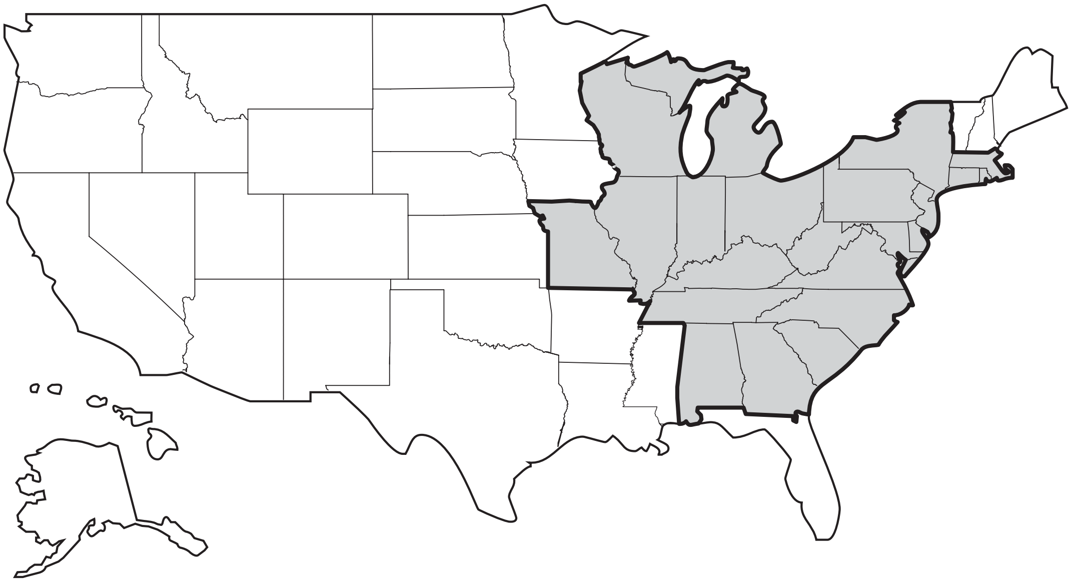


Figure 1-1. States and territories originally subject to NO_X SIP call

SECTION 126 PETITIONS

In 1997, eight northeastern states filed petitions with EPA to reduce the transport of ground-level ozone by asking EPA to find that certain utilities and other sources of NO_X significantly contribute to ozone problems in the eight petitioning states. EPA granted petitions in four of the states by finding that certain large electric utilities and large industrial boilers and turbines violate a Clean Air Act prohibition against significantly contributing to air pollution in other states. As a result of granting the petition, certain facilities will participate in a federal NO_X emissions cap-and-trade program. Sources must implement controls or use emission allowances to achieve their required NO_X emission reductions by May 1, 2003.

1.1.3 $PM_{2.5}$ NAAQS and Regional Haze

The control of NO_X will be one of the important elements in the development of controls of $PM_{2.5}$. NO_X (along with SO_2 and VOCs) are the main precursors contributing to the formation of these very small particles in the atmosphere. Nitrates, compounds that form from NO_X, are one of the constituents of $PM_{2.5}$ and one of the groups of chemicals that are believed to cause adverse health effects. Figure 1-2 shows the constituents that comprise $PM_{2.5}$ in the eastern half of the United States. Small particles formed by reactions of NO_X contribute to the formation of regional haze.

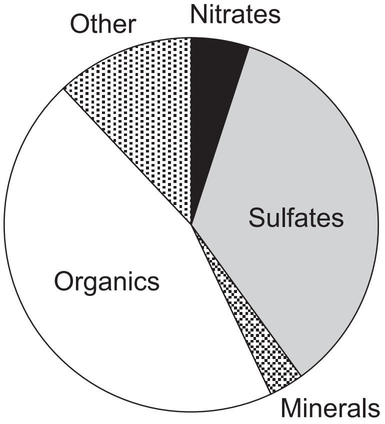


Figure 1-2. Constituents that comprise $PM_{2.5}$ in the eastern half of the U.S.

1.1.4 Acid Rain

Nitrates that form in the atmosphere from NO_X compounds are captured as small particles or as dissolved acid in rain or mist. The nitrates that are deposited in soils can affect the pH of the soils and the uptake of nutrients. Nitrates that reach surface waters such as rivers and lakes increase the nitrogen content of the water. This nitrification process affects the growth of algae and other organisms that can affect aquatic life.

1.1.5 Stratospheric Ozone

Compounds related to the emissions of NO_X, such as N_2O, can reach the stratosphere. In the stratosphere these compounds participate in chemical reactions resulting in the depletion of the protective stratospheric ozone layer necessary to minimize the penetration of UV light. Decreased NO_X emissions will result in decreased emissions of N_2O. Consequently, control of NO_X emissions is important in this regulatory program.

In summary, there are five main issues (NO_2 NAAQS, Ozone NAAQS, $PM_{2.5}$ NAAQS, Regional Haze, and Acid Rain) presently driving environmental programs toward considerably more stringent NO_X control than has been required from past regulatory programs. These regulatory programs related to NO_X emissions are discussed in detail in Chapter 4, *NO_X Regulatory Programs.*

1.2 DEFINITION OF NITROGEN OXIDES

1.2.1 Nitric Oxide and Nitrogen Dioxide

Nitrogen oxides include both nitric oxide (NO) and nitrogen dioxide (NO_2). These are the two primary constituents of NO_X in the effluent gas streams of stationary sources and mobile sources. NO is the main form of NO_X emitted by emission sources. As shown in Figure 1-3, up to 95% of the total NO_X emissions can be in the form of NO.

> NO and NO_2 are formed simultaneously in combustion processes and other high temperature operations.

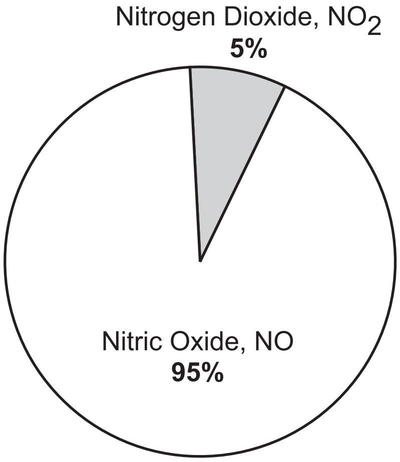


Figure 1-3. Typical NO-NO_2 emission ratios from combustion sources

It is important to recognize that NO and NO_2 are not independent chemical compounds. NO is oxidized in the atmosphere relatively rapidly to form NO_2 by two general reaction mechanism routes. During daytime hours, NO reacts in a complex set of photochemically initiated reactions to produce NO_2. Figure 1-4 demonstrates the rate and extent of conversion of NO to NO_2.

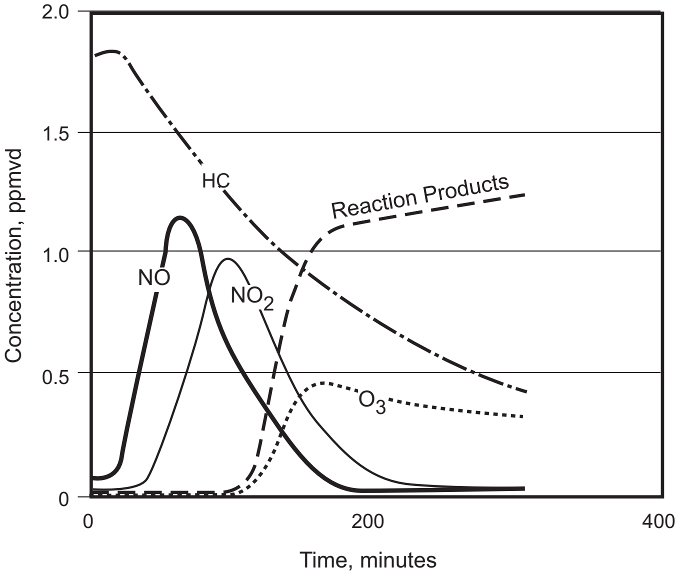


Figure 1-4. Photochemical profile

Figure 1-4 shows the conversion of NO emitted mainly from automobiles during morning rush hour. Time expressed in minutes is shown on the x-axis. The concentration of NO, NO_2, and ozone are shown on the y-axis. The presence of organic compounds and carbon monoxide contributes to the photochemically initiated conversion of NO to NO_2.

The formation of ozone and other photochemical smog constituents increases rapidly as the NO_2 concentration peak is reached. Eventually the NO_2 reacts further to yield a variety of gas phase and particulate phase smog-related compounds. NO_X emissions from motor vehicles and stationary sources outside metropolitan areas also react in similar photochemically initiated reactions. These photochemically initiated reactions of NO_X compounds emitted in both metropolitan and rural areas can continue to form ozone over periods of hours to days as air masses travel over multi-state areas.

These reactions contribute to the regional nature of ozone levels. NO and NO_2 emitted from motor vehicles and stationary sources can also react after being absorbed into small water droplets present in the atmosphere as clouds or fog. These reactions further contribute to the regional nature of ozone formation and transport. For these reasons, the total NO_X emissions from a source are calculated on an NO_2 basis, as if all the NO converts immediately to NO_2. While this is not strictly true from a chemical standpoint, it is a useful regulatory tool to assess total NO_X emissions.

1.2.2 Dinitrogen Tetroxide

The term NO_X also includes dinitrogen tetroxide (N_2O_4). This compound is in constant equilibrium with NO_2 as indicated by the chemical reaction shown in Figure 1-5. At high temperatures the NO_2 form is favored, while at ambient temperatures most of the NO_2 is in the dimer form (N_2O_4). Because of this equilibrium condition, NO_2 cannot be considered separately from N_2O_4. In other words, where NO_2 is present, there is also some N_2O_4. For this reason, N_2O_4 is inherently part of NO_2.

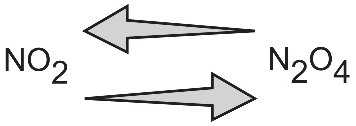


Figure 1-5. Nitrogen dioxide equilibrium with dinitrogen tetroxide

The properties of NO_2 and N_2O_4 are very similar. Both compounds readily absorb light in the ultraviolet (UV) range and can, therefore, participate in photochemical reactions that ultimately yield ozone and other compounds. Both NO_2 and N_2O_4 are moderately soluble in water. They can readily absorb into rain and cloud droplets and ultimately can be absorbed into plants. The primary difference between NO_2 and N_2O_4 is their color. NO_2 is colorless and N_2O_4 has a reddish brown color often associated with photochemical smog.

Both NO_2 and N_2O_4 are primarily formed in the atmosphere. Only small quantities are emitted directly from stationary and mobile sources. NO is the main form of NO_X emitted from fossil fuel-fired boilers.

Nitric oxide (NO), the other main constituent of NO_X, has entirely different chemical and physical properties than NO_2 and N_2O_4. NO is colorless, insoluble and does not absorb UV light. Therefore, NO cannot initiate photochemical reactions. However, NO is a very reactive compound in the atmosphere and reacts rapidly in a photochemical reaction started by even small quantities of NO_2 and other light absorbing compounds present in the atmosphere.

1.2.3 Nitrous Oxide

NO, NO_2, and N_2O_4 are not the only oxidized forms of nitrogen in the ambient air. Small quantities of nitrous oxide (N_2O) can be emitted from both *anthropogenic* (man-made) and natural sources. N_2O that reaches the stratosphere can cause depletion of the protective ozone layer.

Nitrous Oxide (N_2O)
Sometimes called *laughing gas*, N_2O is often not included in discussions of NO_X. N_2O is slightly soluble in water, does not absorb UV light, and is stable at atmospheric conditions. Therefore N_2O does not participate in photochemical reactions that produce ozone and other compounds.

N_2O is formed in the early stages of combustion rather than by atmospheric reactions involving NO and NO_2 emissions. Because of the unstable nature of N_2O at high temperatures, it is rapidly destroyed in the flame zone of combustion, and only small quantities are emitted into the atmosphere. Coal-fired combustion processes have high combustion zone temperatures and, therefore, generally release only a few parts per million (ppm) of N_2O. Low temperature combustion processes, such as fluid bed combustors, can release 70 to 200 ppm N_2O.[2]

Selective catalytic reduction (SCR) systems are another possible source of N_2O. SCRs are NO_X post-combustion treatment systems that introduce chemicals such as urea or ammonia; N_2O can form as a by-product of these reagents.

Once in the atmosphere, N_2O is very stable with a half-life of more than 100 years. Most N_2O remains in the atmosphere until it is dissociated in the stratosphere. Upon dissociation, N_2O breaks the chemical oxygen bonds of O_3 and reduces the amount of UV-protecting stratospheric ozone. N_2O is classified as a greenhouse gas due to its stratospheric ozone-depleting characteristics.

1.2.4 Nitrous Acid and Nitric Acid

A variety of other oxidized nitrogen compounds form in the atmosphere because of photochemical reactions. These include nitrous acid (HNO_2) and nitric acid (HNO_3). Neither of these is considered a NO_X compound because they are not emitted in significant quantities from stationary sources. However, these compounds are environmentally important because both can form in the atmosphere, absorb UV light, and continue photochemical reaction processes. Furthermore, HNO_3 can have a detrimental effect on waterways and plants.

HNO_3
HNO_3 is directly emitted into the atmosphere in relatively small quantities from nitric acid plants and other types of industrial processes involving the generation or use of nitric acid. Approximately 70% of HNO_3 produced is used in the manufacture of ammonium nitrate (NH_4NO_3) used in fertilizers.[2]

1.3 ORIGINS OF NO_X

Origins of NO_X
Low concentrations of NO_x are present in the atmosphere due to natural biological activity (microorganisms) and natural occurrences such as lightning and volcanoes. When low levels of organic compounds and carbon monoxide are also present due to natural activities, the NO_x compounds begin to react in the atmosphere to yield low concentrations of aerosols and a variety of oxidized inorganic and organic nitrogen compounds. The blue haze that is often present in the Great Smoky Mountains of North Carolina and Tennessee is a good example of the naturally occurring NO_x atmospheric reaction products.

Human (anthropogenic) activities substantially increase the quantities of NO_x present in the ambient air. The major NO_X sources include mobile sources such as cars and trucks and large stationary combustion sources such as boilers, incinerators, and industrial furnaces. Ambient levels of nitrogen oxides due to these emissions are typically not sufficiently high enough to pose a *direct* threat to public health. The emissions of NO_x are of concern because NO_x participates in a number of atmospheric reactions with other anthropogenic emissions, such as volatile organic compounds, carbon monoxide, and sulfur dioxide. These reactions result in the formation of ozone (O_3) and particulate matter commonly termed *smog*. NO_x is an especially important reactant in these chemical reaction mechanisms because NO_2, one of the main components of NO_x, absorbs the ultraviolet light and initiates the photochemical mechanisms that contribute to ozone and smog.

Review Exercises

1. Which of the following is a characteristic of nitric oxide?
   (Select all that apply)
   a. Insoluble
   b. Stable in the atmosphere
   c. Reddish-brown coloration
   d. Absorbs ultraviolet light
   e. Possesses a sharp acrid odor

2. Nitrogen dioxide accounts for approximately what percentage of NO_X emissions from combustion sources?
   a. 100%
   b. 95%
   c. 75%
   d. 50%
   e. 5%
   f. 0%

3. Which of the following regulatory programs are currently driving the control of NO_X emissions?
   (Select all that apply.)
   a. NO_2 NAAQS
   b. Ozone NAAQS
   c. Acid Rain
   d. $PM_{2.5}$
   e. Regional Haze
   f. Stratospheric Ozone
   g. All of the above

4. Which of the following pollutants are capable of initiating photochemical reactions?
   (Select all that apply.)
   a. NO
   b. NO_2
   c. HNO_3
   d. N_2O
   e. N_2O_4
   f. None of the above

References

---

[1] Federal Register, October 27, 1998 (63 FR 57356).

2 NO_X Formation in Combustion Processes

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Describe the three types of NO_X formation mechanisms and the relative contributions of each.
2. Describe the importance of temperature on the Zeldovich mechanism.
3. State the parameters that affect the type and quantity of NO_X formed during combustion.
4. Explain the relationship of NO_X to different types of fuel.
5. Identify the possible paths of NO_X formation caused by fuel nitrogen.

2 NO_X Formation in Combustion Processes

2.1 INTRODUCTION

Nitrogen oxides (NO_X) are involved in many regulatory areas and, although it is not the primary pollutant of concern in many of these regulatory areas, it plays an important role. These programs are the basis for controlling NO_X emissions. NO_X plays a role in the following regulatory programs:

- Acid rain
- Forest damage
- Ozone non-attainment
- NO_2 health effects
- Fine PM
- Visibility

The following compounds comprise the category of NO_X:

- Nitric oxide (NO)
- Nitrogen dioxide (NO_2)
- Nitrous oxide (N_2O)
- Dinitrogen trioxide (N_2O_3)
- Dinitrogen tetroxide (N_2O_4)
- Dinitrogen pentoxide (N_2O_5)

In addition to these six compounds, nitrate radicals (NO_3) are also known to occur in the atmosphere.[1]

Nitric oxide (NO) and nitrogen dioxide (NO_2) are the two main pollutants of concern. NO is emitted mainly from stationary combustion sources. Over 90% of the NO_X emitted from stationary combustion sources is in the form of NO. NO_2 is formed in the atmosphere from the NO that is released from the stack. Less than 5% of the NO_X emitted from stationary combustion sources is emitted as NO_2.

Another NO_X compound, nitrous oxide (N_2O) — or laughing gas — is a very stable compound with a half-life of over 100 years. Although it is emitted in small quantities, it migrates to the stratosphere and participates in depletion of the stratospheric ozone layer. It also was once thought to be a problem from coal combustion, but current data indicates that it is emitted at levels below 5 ppm. N_2O is formed in the early stages of combustion, but is subsequently destroyed rapidly at high temperatures. For that reason, N_2O is not an emission of concern from conventional power plants and conventional fossil fuel-fired sources. Emissions of N_2O are more of a concern from low temperature processes such as fluidized bed combustion, where the destruction of N_2O is much slower. Emissions from these low temperature operations can range from 70 to 200 ppm. There is also concern about possible formation of N_2O from flue gas treatment systems based on selective catalytic reduction (SCR). The use of certain materials such as cyanuric acid and urea can contribute to the formation of N_2O.

2.2 NO_X FORMATION MECHANISMS IN COMBUSTION PROCESSES

During combustion, three complex chemical reactions form NO_X. The most important of these is *thermal NO_X* formation. In thermal NO_X formation, NO_X is formed by the reactions of N_2 from the combustion air with reactants such as O and OH radicals and molecular NO_2 . Thermal NO_X is the primary source of NO from stationary combustion sources.

Fuel NO_X is formed when the nitrogen bound in the fuel is combusted. Obviously, the amount of NO_X formed from this mechanism is a function of the fuel being combusted. Natural gas has no fuel nitrogen, and therefore no NO_X is formed by this formation mechanism from the combustion of natural gas. The amount of NO_X formed by the fuel NO_X mechanism in the combustion of fuel oil depends on the type of oil being burned. Heavy oils tend to have higher nitrogen content than light oils such as residential heating oil. The fuel NO_X reaction mechanism is of most concern when coal is being burned.

Prompt NO_X, the third formation mechanism, forms NO_X by converting molecular nitrogen to NO via intermediate products. This reaction occurs in the early phase in the flame front with hydrocarbons.

Emissions of a typical coal-fired boiler include about 75% thermal NO_X and approximately 25% fuel NO_X.[1] Prompt NO_X formation is important to the operation of gas turbines. For fuel oil, NO_X emissions include an average of 45% fuel NO_X. Emissions from gas-fired units are almost entirely comprised of thermal NO_X.[2]

2.2.1 Thermal NO_X

Thermal NO_X is formed from the reaction of nitrogen and oxygen supplied by the combustion air stream and is highly dependent on temperature.

Although oxygen concentration and residence time influence the formation of thermal NO_X, temperature is by far the parameter that most influences the formation of thermal NO_X. The formation of NO_X through the thermal NO_X mechanism has a slow reaction time and, therefore, requires time for equilibrium to be reached.

Figure 2-1 demonstrates the relation of thermal NO_X formation and temperature. This figure shows that the formation of thermal NO_X peaks between 1900°C and 2000°C. Because this is the temperature range in which most stationary combustion sources operate, it is easy to understand that thermal NO_X is the main mechanism by which NO_X is formed in combustion processes.

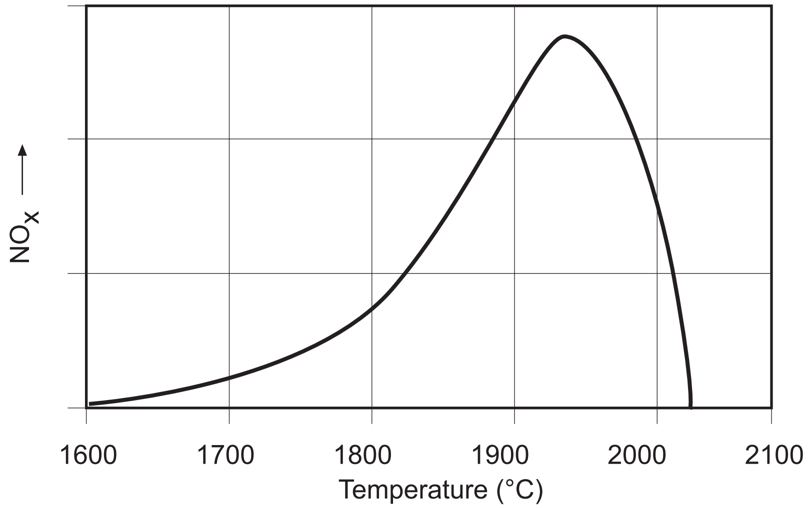


Figure 2-1. Relation of thermal NO_X formation and temperature

NO and NO_X generated from atmospheric nitrogen are often termed *thermal NO_X* because they are formed in high temperature areas of the combustion system. Atmospheric nitrogen (N_2) and oxygen (O_2) entering the combustion zone as combustion air are thermally fixated to form NO_X. The overall stiochiometry is shown in global Reaction 2-1.

$$N_2 + O_2 \longleftrightarrow 2NO \qquad \text{Reaction 2-1}$$

Although Reaction 2-1 provides a simplified summation of thermal NO_X formation, the direct reaction of molecular nitrogen and molecular oxygen is too slow to account for the thermal NO_X mechanism.

In 1946 Zeldovich proposed a reaction mechanism to account for the formation of thermal NO_X.[3] Although many reactions are involved, the basic Zeldovich mechanism reactions can be summarized as follows:

$$N_2 + O \longleftrightarrow NO + N \qquad \text{Reaction 2-2}$$

$$N + O_2 \longleftrightarrow NO + O \qquad \text{Reaction 2-3}$$

$$N + OH \longleftrightarrow NO + H \qquad \text{Reaction 2-4}$$

Reactions 2-2, 2-3, and 2-4 are based on the condition that C, H, O, and OH have reached equilibrium for the combustion reactions. Reaction 2-2 is considered the rate-limiting step because of its large activation energy (317 kJ/mol).[4] In near-stoichiometric and fuel-rich combustion zones, Reaction 2-4 becomes the primary source of NO.[5] Thermal NO_X formed by this mechanism is extremely temperature sensitive as shown in Table 2-1.

Table 2-1
Equilibrium Concentrations of NO and NO_2 in Air and Flue Gas

Temperature (°F)	Air (ppm)		Flue Gas (ppm)	
	NO	**NO_2**	**NO**	**NO_2**
80°F	3.4×10^{-10}	2.1×10^{-4}	1.1×10^{-10}	3.3×10^{-5}
980°F	2.3	0.7	0.8	0.1
2060°F	800	5.6	250	0.9
2916°F	6100	12	2000	1.8

Note: Calculations are based on the reactions $N_2 + O_2 \leftrightarrow 2NO$ and $NO + □O_2 \leftrightarrow NO_2$ with a gas containing 76% N_2 and 3.3% O_2.[2]

Table 2-1 is based on theoretical calculations. As stated in Chapter 1, flue gas NO_X concentrations from combustion sources consist of 90% to 95% NO. The difference can be attributed to a variety of factors, including the Zeldovich Mechanism.

A large amount of energy (941 kJ/mol) is required to break the N_2 molecular bond. The rate of formation in Reaction 2-2 becomes significant at temperatures greater than approximately 2700°F (1500°C).

The vast majority of thermal NO_X is formed in the highest temperature regions of the combustion zone. The global reaction (Reaction 2-1) proceeds rapidly in the forward direction at high temperatures. Once the gas begins to cool, the reaction reverses. The reverse reaction is pre-empted because of the required radicals (C, H, O and OH) and activation energy. The NO_X levels become "frozen," since Reaction 2-1 is not allowed to proceed in the reverse reaction.

The main factors affecting the quantity of NO_X formed by thermal fixation are (1) the flame temperature, (2) the residence time of the combustion gases in the peak temperature zone of the flame and, to a slightly lesser extent, (3) the amount of oxygen present in the peak temperature zone of the flame. (Combustion modifications are discussed in Chapter 6.) Thermal NO_X reduction is therefore accomplished by various combustion modification techniques such as the use of low excess air, staged combustion, reduced air preheat, or flue gas recirculation.

Techniques for controlling or minimizing the formation of NO_X through the thermal NO_X mechanism include: (1) reducing the local oxygen concentration at the peak flame temperature, (2) reducing the residence time at the peak flame temperature, (3) maintaining peak flame temperatures to below 1300°C, and (4) decreasing the furnace release rate. The theory of this last control method is to remove the reactants from the reaction zone into the lower temperature ranges before equilibrium is reached, so that less NO is formed.

2.2.2 Fuel NO_x

NO_X generated from organically bound nitrogen contained in fuel is termed *fuel* NO_X. The oxidation of nitrogen compounds contained in fossil fuels can create appreciable concentrations of NO and NO_2.

Although thermal NO_X typically accounts for the majority of NO_X emissions, fuel NO_X has been observed in certain cases to account for over 40% to 50% of the emissions. In addition, fuel NO_X can represent more than half the NO_X emissions for residual oil fuel.[1]

This variation in the quantity of NO_X emissions generated from the fuel NO_X mechanism is because fuel NO_X formation is related to the nitrogen content of the fuel. The extent of the conversion of nitrogen in the fuel to NO_X *decreases* as the nitrogen content of the fuel *increases*.

Coal and oil are sources of fuel NO_X. U.S. hard coals contain approximately 0.2 wt-% to 3.5 wt-% nitrogen.

Anthracite coals constitute the low end, while bituminous coals make up the high end of this range. In general, oils contain from 0.01 wt-% to 0.5 wt-% nitrogen.[1]

Upon distillation, nitrogen tends to accumulate in the heavy resins and asphalt fractions of petroleum. In North America, a nitrogen content of above 0.3% is common for most heavy residual oils. Natural gas contains no organically bound nitrogen, and therefore does not yield fuel NO_X.

Fuel NO_X formation is also dependent on the oxygen levels in the vicinity of the flame. Consequently, the reduction of oxygen levels is an important factor in reducing levels of NO_X emissions that are formed from the fuel NO_X mechanism. It is important to note that the oxygen level in the flame zone is as important as the average oxygen concentration in the combustion chamber.

The precise mechanism for all fuel NO_X formation is not well understood. However, the conversion of nitrogen in coal is generally clear. The volatile fraction and char combustion mechanisms are both important in the conversion of coal-bound nitrogen to NO_X.

Within the first 300 milliseconds of combustion, the volatile species containing a portion of the coal-bound nitrogen are vaporized and combusted homogeneously. During the volatilization conversion, the remaining N is retained in the char. Char N is also a source of NO_X. The possible paths of fuel nitrogen in coal particles are shown in Figure 2-2.

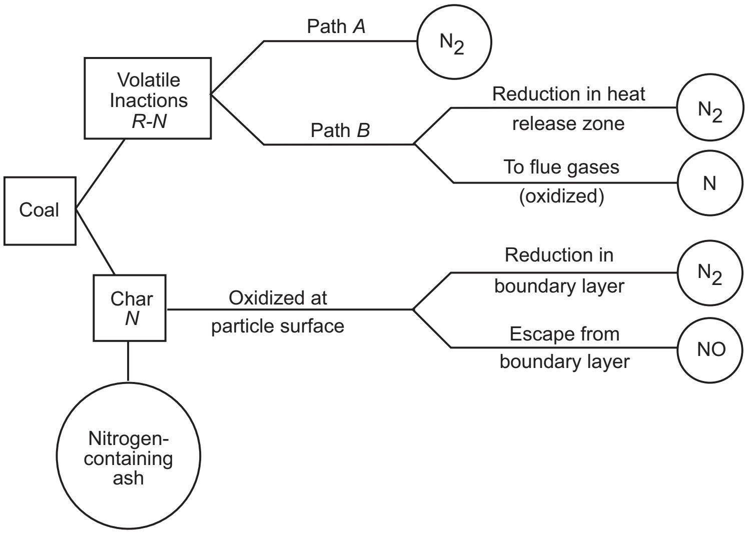


Figure 2-2. Possible paths of fuel nitrogen contained in coal particles during combustion[3]

Volatile Fraction

Approximately 60% to 80% of fuel NO_X can be attributed to volatile nitrogen combustion.[3]

The conversion rate of volatile nitrogen to NO_X increases with the combustion zone temperature. In other words, lower temperatures result in a lower amount of fuel nitrogen devolatilization. This is the reason why fluidized bed combustors are inherently low NO_X emitters compared to conventional sources.

Coal nitrogen devolatilization occurs prior to oxidation in fuel-rich zones when fuel droplets or particles are heated. Devolatilization forms a number of intermediate radicals, such as HCN, N, CN, NO_X and NH. These intermediate radicals are either oxidized to NO or they form N_2. The dominant radical for reaction is dependent on the form of the fuel nitrogen in the fuel. Aromatic or cyclic nitrogen is believed to result in the intermediate product hydrogen cyanide (HCN) from the volatile fraction that oxidizes to form NO and NO_2. Ammonia has been shown to be the intermediate radical when the fuel nitrogen is in the form of aliphatic amines. The series of reactions involved in fuel NO_X formation is extensive and complex. Presentation of the detailed reactions involved in fuel NO_X mechanisms is beyond the scope of this manual.

Char Combustion

Char combustion refers to the conversion of nitrogen contained in char to either NO or N_2 by heterogeneous reactions in the post-combustion zone. The char combustion process is slower than the coal nitrogen devolatilization process. Therefore, formation of NO is approximately 2.5 times greater for volatile nitrogen combustion compared with char combustion.

Char material is formed by rapid pyrolysis of fuel particles. Char material remains after following oxidation and consists of a mass of pure carbon or carbon monoxide. Reactions take place at the surface of the char particle where oxygen concentration is the highest. Within a thin boundary layer that surrounds the particle, gas velocity approaches zero and gaseous mixing is often poor.

Not all of the fuel nitrogen compounds are released during combustion. A significant fraction of the fuel nitrogen remains in the bottom ash or in the fly ash. In fuels that are high in nitrogen content, such as coal and heavy oil, approximately 20% to 60% of the fuel-bound nitrogen is oxidized.[6] The effect of nitrogen content of the fuel on NO_X emissions is shown in Figure 2-3.

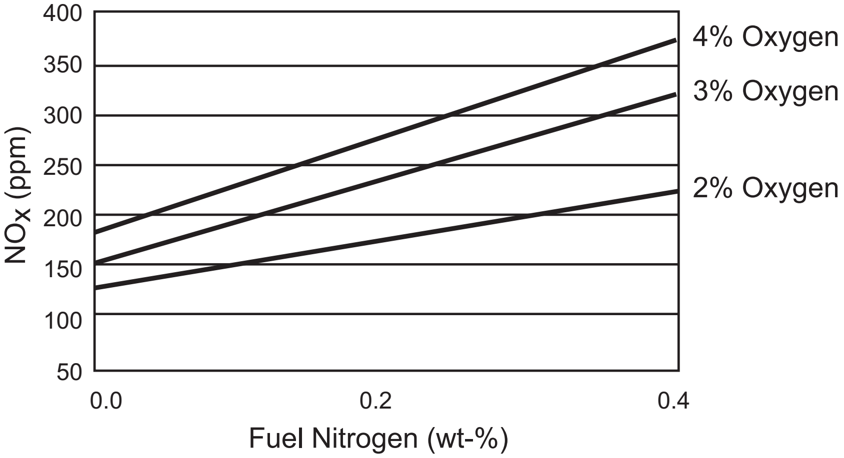


Figure 2-3. Effect of fuel nitrogen on NO_x emissions[7]

The rate of NO_X formation due to fuel nitrogen is strongly affected by the local oxygen concentration present in the flame and by the mixing rate of the fuel and air. Thus, as with thermal NO_X, fuel NO_X is dominated by local combustion conditions. Because of spatial differences of temperature, oxygen and other factors, *local conditions* refers to the conditions at a specific area in the combustion zone. However, fuel NO_X is formed at relatively low temperatures compared to thermal NO_X.

One control option for reducing fuel NO_X emissions is to reduce the nitrogen content in the fuel; however, this is not always possible. Therefore, combustion modification techniques (described in detail in Chapter 6) may be used to reduce NO_X emissions:

- Decrease of combustion temperature
- Decrease of the O_2 partial pressure
- Low excess air firing
- Air preheat (secondary air preheat)
- Low NO_X burner designs
- Staged combustion

2.2.3 Prompt NO_x

Of the three formation mechanisms, prompt NO_X constitutes the smallest source of NO_X. This mechanism has the greatest impact in fuel-rich combustion zones (such as those present in gas turbines) and low temperature combustion processes. The degree of conversion depends on the stoichiometric conditions and temperature.

> Prompt NO_X forms within the first five milliseconds of combustion because of the presence of partially oxidized organic species present within the burner flame. Organically bound nitrogen in the fuel reacts quickly in the presence of free radicals such as HCN, NH, and N. The intermediate compound, HCN, is formed and elemental N is quickly oxidized to form NO_2. Free radicals continue to react and form NO by breaking the N-C bond.

Because the residence time in typical combustion chambers is too short to allow equilibrium to be established, thereby creating high NO_X concentrations, NO_X emissions generated through the prompt NO_X mechanism are of minor importance in large-scale combustion systems.

> Prompt reactions are not sensitive to the peak gas temperature. Therefore, combustion modifications do not have a strong influence on the NO_X formed by this mechanism.

Review Exercises

1. What factors favor the formation of thermal NO_X?
   (Select all that apply.)
   a. High gas temperature
   b. High oxygen concentrations
   c. High residence time at high gas temperature
   d. Flame impingement
   e. All of the above

2. What mechanism generally describes the formation of thermal NO_X?
   a. Homogeneous oxidation mechanism
   b. Zeldovich mechanism
   c. Johnson mechanism
   d. None of the above

3. What fraction of NO_X is generally due to thermal NO_X formation in coal-fired boiler applications?
   a. 95% to 99%
   b. 90% to 95%
   c. 80% to 90%
   d. 50% to 80%
   e. 20% to 50%
   f. 1% to 20%

4. What is the typical wt-% fraction of fuel nitrogen in coal?
   a. 0.2% to 3.5%
   b. 0.1% to 0.2%
   c. 0.01% to 0.1%
   d. None of the above

5. Which fossil fuel has nearly negligible levels of fuel nitrogen?
   a. Residual oil
   b. Distillate oil
   c. Natural gas
   d. Wood
   e. None of the above

References

---

[1] U.S. Environmental Protection Agency, Office of Air and Radiation. August 1997. *Nitrogen Oxides: Impact on Public Health and the Environment.* Research Triangle Park, NC.

[2] Pakrasi, A., and Davis, T.D. 2000. *Combustion Sources Air Pollution Engineering Manual.* 2nd Edition. John Wiley & Sons. New York, NY.

[3] Cooper, C.D., and F.C. Alley. 1986. *Air Pollution Control: A Design Approach.* Waveland Press, Inc. Prospect Heights, IL.

[4] U.S. Environmental Protection Agency. January 1983. *Control Techniques for Nitrogen Oxides Emissions from Stationary Sources*. Revised Second Edition. EPA-450/3-83-002.

[5] U.S. Environmental Protection Agency. 1980. *Controlling Nitrogen Oxides.* U.S. EPA Publication 600/8-80-004.

[6] U.S. Environmental Protection Agency. 1980. *Controlling Nitrogen Oxides.* U.S. EPA Publication 600/8-80-004.

[7] U.S. Environmental Protection Agency. November 1977. *Technical Assessment of* NO_X *Removal Processes for Utility Application.* U.S. EPA 600/7-77-127.

3 NO_X Emission Trends and Sources

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Name the five anthropogenic source categories that contribute the most NO_X emissions.
2. Describe how the Clean Air Act Amendments of 1970 affected NO_X emission trends.
3. Distinguish between biogenic and geogenic NO_X sources.
4. Identify at least four natural sources of NO_X emissions and their relative contributions of NO_X emissions.

3 NO_X Emission Trends and Sources

All of the information on NO_X emissions that is presented in the video-based portion of this chapter is taken from the data in the 1996 National Emission Trends Inventory (NET). The NET is a comprehensive inventory that contains EPA's latest estimates of nationwide emissions of NO_X, VOC, CO, SO_2, PM_{10}, $PM_{2.5}$, and NH_3.

> More current information from subsequent trend reports is interjected throughout this manual.

The NET contains trends data on emissions, emission activities, and emission control programs. Data contained in the NET dates back to 1985. NET also contains pre-1985 data; however, that data is less detailed than the post-1985 data and is available only in 10-year increments.

In terms of temporal and spatial allocation, data in the NET is tracked annually as well as on an *ozone season daily basis*. An ozone season daily basis means that emissions are tracked on a daily basis on the days that occur during the warmest period of the year. The spatial inventory is a very detailed inventory and, for large stationary sources, contains unit level emissions for every stationary source in the country. For smaller stationary sources and mobile sources, the NET contains county level emissions data.

Sources of NO_X have been characterized in the NET according to the following major source categories:

- Electric generating units (EGUs)
- Non-EGU point sources
- Stationary area sources
- Nonroad mobile sources
- Highway mobile
- Biogenics

Each of these major source categories is discussed separately in the following sections.

3.1 ANTHROPOGENIC SOURCES

Anthropogenic sources include a wide variety of power generation units, industrial manufacturing facilities, motor vehicles, and other transportation sources. The locations of these sources are closely related to population density as indicated in Figure 3-1. The highest concentration of sources in the U.S. is in the northeast, southeast, midwest, and Pacific coastal regions.

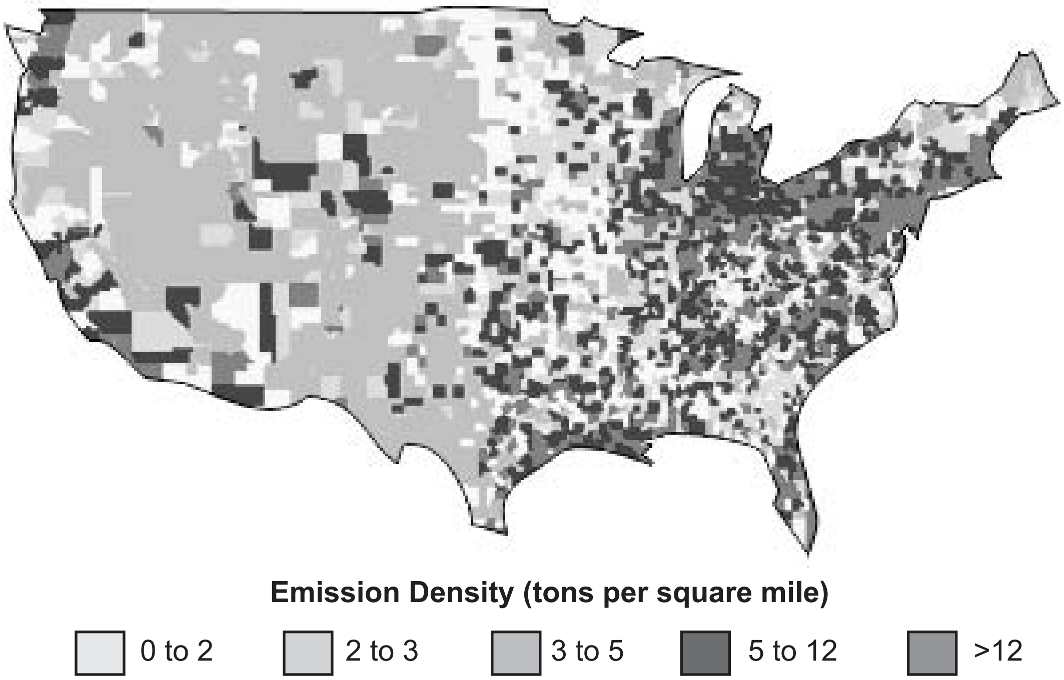


Figure 3-1. Geographic distribution of anthropogenic sources[1]

Anthropogenic NO_X emissions are primarily generated by fuel burning systems. More than 23 million tons of NO_X is emitted into the atmosphere each year as a result of burning fossil fuels.[1] These sources can create local ambient NO_X levels that are ten times greater than those created by natural sources.

Figure 3-2 shows the major sources of anthropogenic NO_X emissions. The leading contributors of anthropogenic NO_X emissions are vehicles and electric generating units (EGUs).

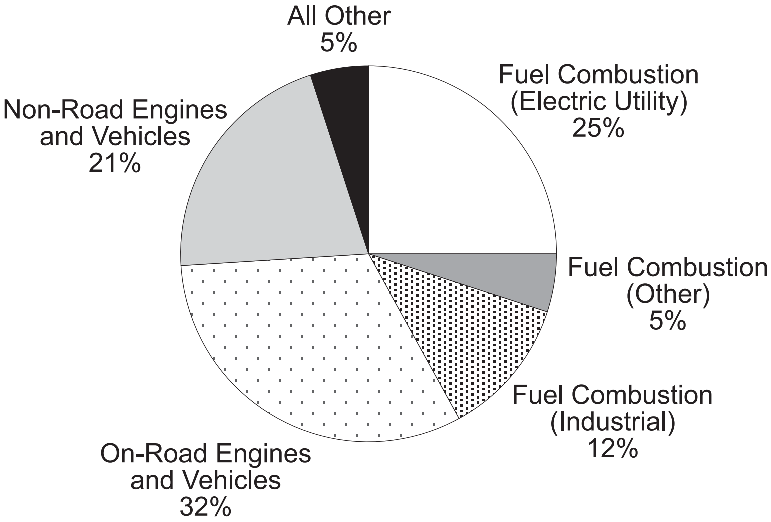


Figure 3-2. Major sources of anthropogenic NO_x emissions[1]

3.1.1 Electric Generating Units

As indicated in Figure 3-2, the EGU emissions represent approximately 25% of the total U.S. anthropogenic emissions. Electric generating units (EGUs) are defined as combustion sources that produce electricity for sale to a power pool or grid under contract.[2] EGUs are all point sources and are classified as steam and non-steam generating boilers. Steam generating boilers include large stationary coal-, gas-, oil-, and wood-fired electric utility units. Non-steam generating boilers include gas turbines and internal combustion engines.

> Approximately 6.1 million tons of NO_X (as NO_2) was emitted from EGUs in 1998. Approximately 90% of this amount was contributed by coal-fired sources.[2] For the coal-fired EGUs, 65% of NO_X emissions resulted from the burning of bituminous coal, while 30% came from the burning of sub-bituminous coal.[3] The remaining 5% resulted from the burning of anthracite coal and lignite.[2] This source category is the largest emitter of anthropogenic NO_X. EGUs are located throughout the U.S.

The data that are contained in the NET comes from a number of data sources. The best source of data is the EPA Acid Rain Division's Emission Tracking System (ETS). As part of the Clean Air Act Amendments of 1990, large combustion sources are required to install continuous emission monitors (CEMs) that continuously record both heat input and emissions data. This CEM data is augmented with data from the Department of Energy. Specifically, utilities are required to report fuel use data using EIA form 767. The fuel use data contained in the EIA 767 report is used to generate emissions data. Data can also come directly from the facilities when the CEM data or the EIA 767 data contain errors. Several emission estimation techniques or algorithms are used to convert the data in the ETS/CEM database to terms of pounds or tons of emissions.

The National Allowance Data Base is another source of NO_X emissions data. Emissions data in this database are mainly generated by using fuel use data and applying standard emission factors to calculate emissions. Emissions data are also generated from stack test data. However, stack test data are available only on an *ad hoc* basis when industrial facilities provide such data. In general, emission estimates from EGUs are generated by a bottom-up technique that uses data at the lowest level of detail and works up to the next level.

3.1.2 Non-EGU Point Sources

Non-EGU point sources include large sources that can be classified as either non-EGU fuel combustion sources or industrial processes.

3.1.2.1 Industrial Fuel Combustion Sources

Industrial fuel combustion sources include numerous small-to-moderate sized boilers used to generate steam and/or electricity for use on site at the facilities. This category also includes cement and lime kilns, industrial furnaces, and other industrial processes using burners for process heat. The dominant fuels used for industrial boilers and industrial furnaces are coal, oil, gas, coke, and wood. Collectively, non-EGU industrial boilers and industrial furnaces are responsible for approximately 12% (3.0 million tons per year) of the U.S. anthropogenic NO_X emissions.[4] Non-EGU industrial boilers and industrial furnaces are located throughout all industrialized areas of the U.S.

3.1.2.2 Industrial Processes

Industrial processes are responsible for 5% (0.9 million tons per year) of annual U.S. anthropogenic emissions.[4] This category is comprised of all non-combustion sources of NO_X and related compounds and includes the following:

- Chemical and allied product manufacturing
- Metals processing
- Petroleum refining and related industries
- Solvent utilization
- Storage and transport
- Waste disposal

Facilities that manufacture or use nitric acid are the main contributors of non-combustion NO_X emissions. Nitric acid is produced for the manufacture of fertilizers (ammonium nitrate), synthetic fibers (adipic acid), explosives (nitrobenzene) or use in metal pickling and etching.

> NO_X emissions from nitric acid facilities differ from combustion sources because they represent a portion of the raw product. For this reason, it is an economic benefit for chemical facilities to recover *significant* NO_X emissions. However, some facilities find material recovery to be impractical, and the product is emitted instead.
>
> In nitric acid manufacturing, concentrations below 1,000 ppm to 3,000 ppm are generally considered too low to recover for economic benefit. In military ordnance works, where large amounts of nitric acid are manufactured for organic nitration, nitric acid concentrations are also considered too low to recover. Therefore, these facilities emit much more NO_X than other non-combustion sources.

The available site-specific emissions data for these non-EGU point sources varies according to the location of the facility. For example, data is available for sources emitting as little as 10 tons per year in certain attainment areas. However, in rural and non-attainment areas, data may be available only for sources emitting more than 100 tons per year. Where facility-secific data is not available, the data for these sources will be included in the *stationary area source* category (to be discussed later).

Non-EGU point sources are responsible for 14% of the total anthropogenic NO_X emissions. Forty percent of total NO_X emissions is emitted from major stationary sources (non-EGU and EGU sources), and most of this amount is generated from combustion processes.

> It should be noted that these percentages differ slightly from the other estimates provided in this chapter. This is because the data on the video is based on 1996 information and the supplemental information in this manual reflects more recent 1998 data.

The NET data for non-EGU point sources have a variety of origins. Data is obtained from emission inventories that are developed by state and local agencies using surveys of industrial facilities. This inventory data is then submitted to EPA.

In addition, several regional programs and studies have been conducted that involve the collection of emissions inventory data. Some examples include the Ozone Transport Assessment Group (OTAG) study of the eastern two-thirds of the United States and a similar study that was conducted in the western U.S. by the Grand Canyon Visibility Transport Commission (GCVTC).

Another source of emissions data for the NET is the Aerometric Information Retrieval System (AIRS) Facility Subsystem. State air agencies routinely report emissions data to AIRS. Finally, emissions data projected from the National Acid Precipitation Assessment Program (NAPAP) also serve as a source of emissions data for the NET.

Emissions are estimated directly from continuous emissions monitor (CEM) data for some of the large point sources. Stack test data (when available) can also serve as a basis for estimating emissions. Another method for estimating emissions is to conduct a materials balance, where the material consumed in a process is subtracted from the material entering the process to obtain an estimate of emissions from that process. However, most emission estimates for non-EGU point sources are derived using emission factors. Emission factors provide an estimate of emissions based on a specific industrial activity (e.g., amount of NO_X emitted per unit of fuel burned). As with the EGU stationary sources, emission estimates are generated using a bottom-up technique.

3.1.3 Stationary Area Sources

Stationary area sources are primarily smaller sources that do not meet the size threshold for reporting emissions individually. This group includes smaller industries, commercial/institutional establishments, and residential sources. The category comprises 11% of anthropogenic NO_X emissions.

> It should be noted that this percentage differs slightly from the other estimates provided in this chapter. This is because the data on the video is based on 1996 information and the supplemental information in this manual reflects more recent 1998 data.

Most of these emissions are associated with “other fuel combustion sources.”

> “Other fuel combustion sources” includes commercial, institutional, residential and miscellaneous fuel combustion sources. Most of the emissions (90%) are from very small sources. NO_X emissions from this category represent 5% (1.1 million tons per year) of the total U.S. anthropogenic NO_X emissions. Figure 3-3 gives a further breakdown of “other fuel combustion sources.”

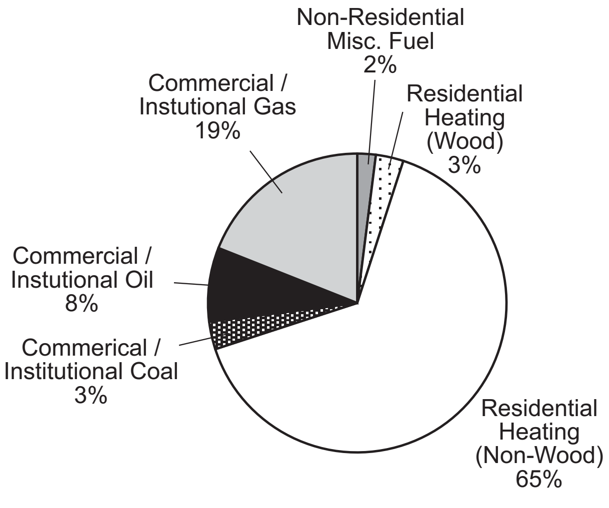


Figure 3-3. Sources of NO_x emissions for the category “Fuel Combustion (Other)” shown in Figure 3-2[1]

It is apparent that residential heating using non-wood fuel (primarily gas and distillate oil) is the dominant NO_X source in this emission category. Commercial/institutional gas heating systems are also major contributors to the NO_X emissions for this source category.

Emissions data in NET for the area source category are obtained through a top-down method. Both demographic and fuel use data are obtained from either the state or national level, and emission factors are applied to generate emission estimates. In addition, EPA has obtained data from some of the regional efforts that were previously discussed (i.e., OTAG, GCVTC, and NAPAP).

Emissions are estimated through a top-down procedure. Emission factors are applied to activity factors at the state level (county level data is used when available) to estimate emissions. In certain urban areas (i.e., urban areas that are non-attainment for ozone) a more detailed emissions inventory may be available and used whenever it is available.

3.1.4 Non-Road Mobile Sources

Non-road mobile sources include the following:

- Aircraft
- Marine vessels (commercial and recreational)
- Railroads
- Lawn and garden equipment
- Logging and construction equipment
- Industrial engines

This category accounts for 19% of anthropogenic NO_X emission sources.

Based on the 1998 Emissions Trends Report, this category comprises 22% (5.3 million tons annual) of anthropogenic NO_X emission sources. The breakdown of non-road mobile emission sources is shown in Figure 3-4. The pie chart on the left presents the contributions for each of the major types of non-road mobile sources. Most of the non-road mobile source NO_X emissions are from diesel engines. The pie chart on the right presents a further breakdown, showing the types of non-road diesel sources.

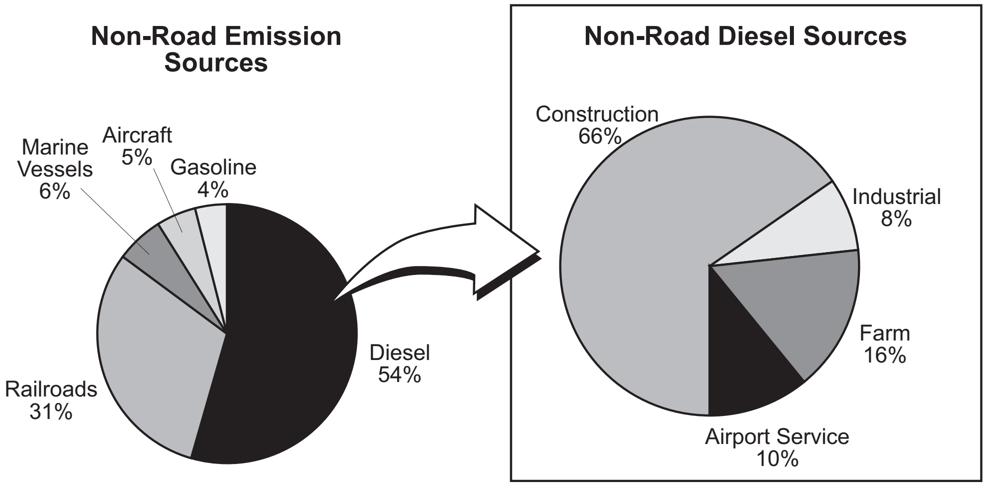


Figure 3-4. Sources of non-road NO_x emissions with detail of diesel source categories[2]

Sources of emissions data for non-road mobile sources in the NET are similar to the sources that are used to obtain emissions data for the stationary source categories. Also similar to stationary sources, the emissions for non-road mobile sources are estimated through a top-down procedure. Bottom-up data is used in those cases where it is available.

EPA's Office of Mobile Sources (OMS) is developing a model that will generate estimates of non-road emissions. This model will allow emissions to be estimated at various geographic levels ranging from a national level to a county level. More information on this model can be obtained from the following website: *www.epa.gov/oms/nonrdmdl.htm*.

> As a part of reorganization in January 2000, EPA's Office of Mobile Sources (OMS) was restructured, placed under new leadership, and given a new name: Office of Transportation and Air Quality (OTAQ). OTAQ includes four program divisions and a consolidated laboratory and support services division. References in the broadcast video or this text to OMS are understood to refer to the current organization, OTAQ.

3.1.5 Highway Mobile Sources

Highway vehicles include passenger cars and trucks, diesel vehicles, pickup trucks and vans, multi-trailer trucks, motorcycles, and sport utility vehicles certified for highway use. Both gasoline- and diesel-fueled vehicles are included in this category which comprises 30% of total U.S. anthropogenic NO_X emissions.

As indicated in Figure 3-2, highway mobile sources are the single largest category of U.S. anthropogenic emissions, representing over 32% (7.8 millions tons annually) of U.S. emissions. [It should be noted that this percentage differs slightly from the other estimates provided in this chapter. This is because the data on the broadcast video is based on 1996 information, and the supplemental information in this manual reflects more recent 1998 data.]

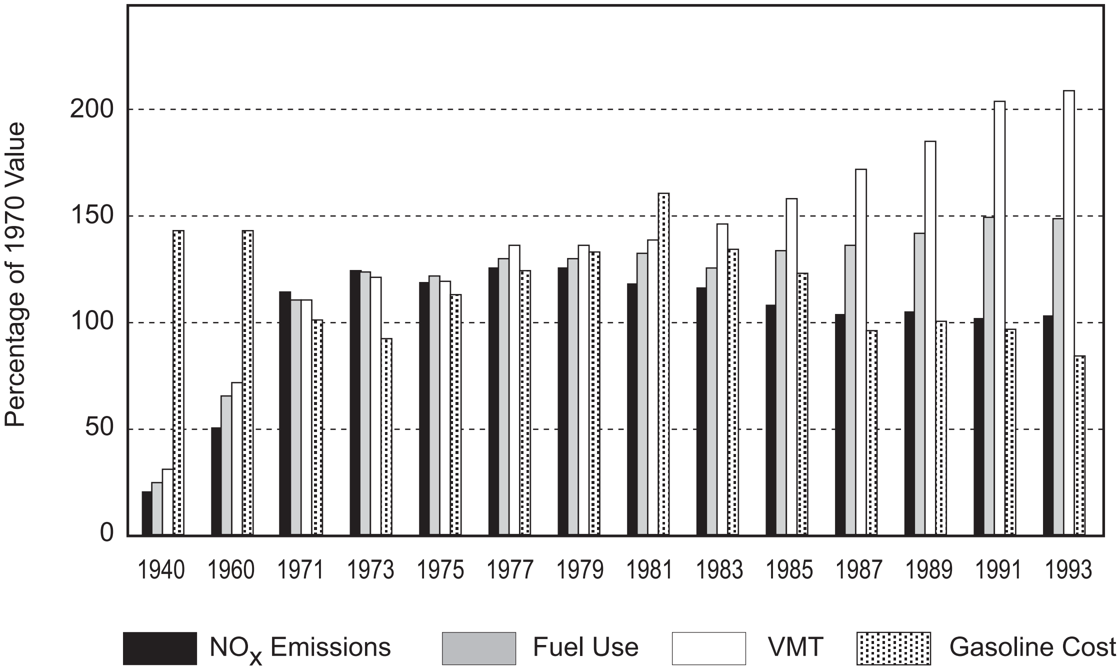


Figure 3-5. Highway mobile NO$_x$ emissions and surrogate indicators[2]

Emissions relative to fuel use, vehicle miles traveled (VMT), and gasoline prices for highway mobile sources are shown in Figure 3-5. It can be seen from the yearly increase of VMT since 1981 that control of mobile source emissions is important in reducing secondary pollutants. The slower increase of fuel use compared to VMT indicates that vehicles built after the 1970s have become increasingly fuel-efficient.

After peaking in 1978, NO$_X$ emissions have gradually decreased as a result of lower emissions per quantity of fuel combusted. Reduced emissions are a result of controlling fuel-air mixture, lower nitrogen containing fuels, exhaust gas recirculation, catalysts, and other engine modifications.

An activity enumerator of vehicle miles traveled is used as the basis for estimating emissions for highway mobile sources. VMT is an estimate of the number of miles that individuals are driving. The Federal Highway Administration (FHA) maintains a national database of VMT as part of the Highway Performance Monitoring System (HPMS). EPA uses this database as the source of VMT data for estimating emissions from the highway mobile source category. Emissions are estimated through a top-down procedure using EPA's Office of Mobile Sources MOBILE5b model. OMS is currently developing a MOBILE6 model. Data such as ambient temperature, fuel type, speed information, vehicle type, registration data and control program information (e.g., inspection/maintenance, reformulation) are fed into the model to generate emission factors that can be applied to the VMT data to calculate emissions.

3.1.6 Miscellaneous Sources

A variety of small combustion sources, small engines, and open burning processes contribute approximately 1% of the total U.S. anthropogenic emissions. Like mobile sources, these sources are classified as *area sources*. Area sources are individual sources that have not been inventoried as specific emission points. Area sources represent a collection of emission points for a specific geographic area, most commonly at the county level.

3.2 NATURAL SOURCES

An understanding of natural sources of NO_X is helpful to refine NO_X control strategies aimed at anthropogenic sources. Unfortunately, natural NO_X emissions are (1) difficult to measure and (2) fluctuate significantly both seasonally and regionally. NO_X, nitric acid, nitrous oxide, nitrates, and ammonia are released into the atmosphere from a variety of sources.

Natural sources of NO_X compounds may be categorized as *biogenic* or *geogenic sources.* Each category is discussed separately in the following sections.

3.2.1 Biogenic Sources

Biogenic sources are those whose emissions result from natural biological activity (i.e., living organisms). Biogenic NO_X emissions can come from soils, forests, and croplands. Some of the main factors that influence the quantity of biogenic emissions that are generated include land use and climatology (i.e., temperature). Biogenic NO_X emissions comprise approximately 6.5% of the total U.S. NO_X emissions or 1.5 million tons NO_X /year.

Sources of information for estimating biogenic NO_X emissions include the U.S. Forest Service, the U.S. Department of Agriculture, the Biogenic Emission Land-Use Database, and U.S. Census Urbanized Boundary data. They provide information such as the type of land coverage (e.g., forest, agricultural, grasslands, and water). EPA uses the land-use data from these and other sources as input to the Biogenic Emissions Inventory System-2 (BEIS-2) to generate estimates of biogenic NO_X emissions.

The biogenic emission estimates have a margin of error of at least 100%.[5] One reason for this uncertainty is the variability between soil types and moisture levels within the same area source boundary. In fact, the emission factors assigned for biogenic soils emissions are assigned an "E" rating. This is the lowest rating for the assessment of the representativeness of emission factors.

One example of a biological activity that generates NO_X emissions is microbiological activity in soil. This is a necessary process in the cycling of nitrogen compounds through the ecosystem. A small amount of NO_X, mostly in the form of NO and NH_3, is a by-product of this process. However, with the addition of fertilizer, the release of nitric oxide and ammonia is greatly accelerated. Natural NO_X emissions from soils have been estimated to contribute as much as 8% of NO_X emissions nationally.[6]

An example of a basic emission rate equation used by computer models for microbial activity in forested areas is shown in Equation 3-1. Emission factors for canopy vegetation (i.e., forests and trees) are generally much greater for VOCs than for NO_X. However, for non-canopy vegetation types, (primarily agricultural crops) emission factors for NO_X can be much higher than for VOCs.

$$ER_i = \sum_{j=1}^{n} \left[A_j \times FF_j \times EF_{ij} \times F(S,T)\right] \qquad \text{Equation 3-1}$$

Where:

ER_i = emissions rate of pollutant i (μg/hr)

A_j = area of vegetation for each vegetation type j (m^2)

FF_j = foliar density factor for each vegetation type j (g leaf biomass/m^2)

EF_{ij} = emissions factor for each chemical species i and vegetation type j (μg/g leaf biomass • m^2)

F(S,T) = environmental factor accounting for solar radiation, S, and leaf temperature, T (dimensionless)

NO_X emissions, mostly in the form of NO, released from the soil are both temporally and spatially variable. NO_X emissions are released at an increased rate during periods of higher solar radiation (i.e., daytime during the summer months) and in areas with greater agricultural activity. The release of biogenic NO_X from soil fluctuates greatly with temperature. In fact, an increase of 10°C can double the biogenic NO_X emissions.[5] Table 3-1 displays the seasonal variance of estimated biogenic NO_X emissions for 1988 through 1996.

Table 3-1
Seasonal Biogenic NO_X Emissions (%)[6]

YEAR	Winter	Spring	Summer	Autumn
1988	11%	23%	42%	24%
1990	15%	21%	39%	25%
1991	12%	24%	40%	23%
1995	12%	22%	41%	24%
1996	12%	23%	41%	24%

Figure 3-6 displays the spatial variation of biogenic NO_X emissions nationwide and shows the impact that land use has on biogenic NO_X emissions. The greater biogenic emission densities in the midwestern states are attributed to high agricultural activity.

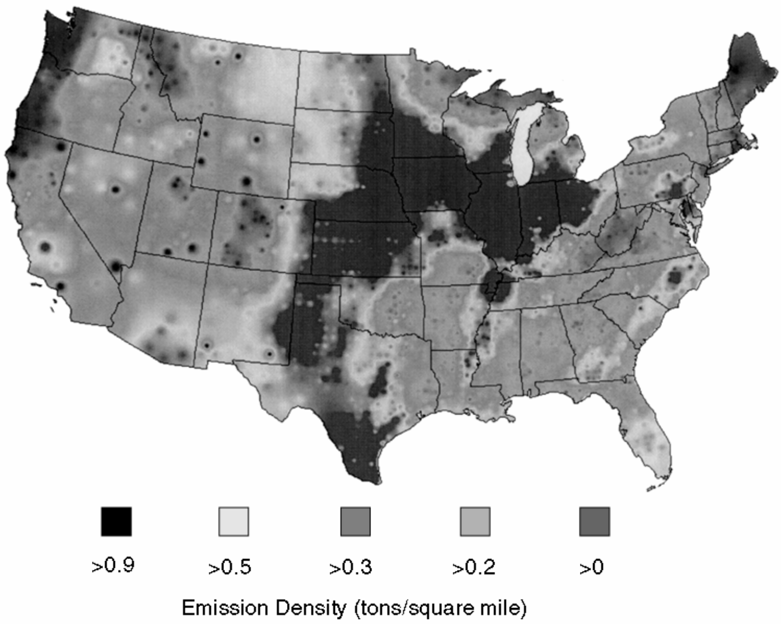


Figure 3-6. Biogenic emission density of NO_x in the U.S.[4]

The information presented in Figure 3-6 is based primarily on the BEISE-2 EPA computer model that takes into account land-use characteristics. There is also a set of emission factors that takes into account climatic conditions.

3.2.2 Geogenic Sources

Geogenic sources of NO_X emissions include:

- Marine ecosystems (NO_X, N_2O)
- Lightening (NO_X, N_2O)
- Material burning (NO_X, NH3)
- Stratospheric intrusion (NO_X)
- Volcanoes and geysers (NO_X, N_2O, NH_3)

Each of these sources is discussed in the following sections.

Geogenic emission estimates are based, in part, on the East Coast Lightening Detection Network, satellite data, the National Lightening Detection Network, and the U.S. Bureau of Economic Activity.

3.2.2.1 Marine Ecosystems

NO_X emissions are released from the ocean as a result of the photolysis of nitrates in saltwater at the ocean surface. The contribution of NO_X by marine ecosystems is small and has minimal impact on atmospheric reactions over landmasses.

3.2.2.2 Lightning

A lightning flash consists of a series of lightning strokes. On average, two strokes occur for every cloud-to-ground flash and six stokes occur for every cloud-to-cloud flash.[7] Although a lightning flash is very short (100 flashes/sec and 0.0001 sec/stroke)[3] the resulting extreme energy and temperature cause NO_X and N_2O formation. An average stroke is 5 km long and yields temperatures of 30,000°K with an energy release of 1.5×10^4 Joules per meter.[7]

There is a great deal of uncertainty concerning NO_X formation due to lightning. Values are based on emission factors that contain a great deal of variability due, in part, to the differences in number of strokes, electrical discharge, stroke length and latitude. The difficulty of measuring NO_X emissions from actual lightning strokes also hinders the development of accurate emissions estimates.

The high temperatures produced during lightning result in the formation of NO from molecular oxygen and nitrogen. Lightning strikes have been estimated to account for as much as 14% of NO_X emissions globally and 4% of NO_X emissions nationally. The accuracy of these values varies because estimations of global NO_X formed due to lightning range from 6.5 to 300 teragrams per year (Tg/yr).[3]

The formation of N_2O from lightning is less significant than NO_X formation. It is estimated that 0.14 grams N_2O are formed for every lightning flash.[7]

Estimates of global contributions of lightning-induced N_2O emissions range from 0.0136 to 0.0998 Tg/yr.[7]

3.2.2.3 Fires

Burning sources include wildfires, prescribed burning, coal refuse fires, agricultural drums, solid waste burning, and structural fires. Emissions from these sources are highly variable and difficult to quantify.

The size, intensity, and frequency of wildfires are dependent on meteorological conditions, types of vegetation, moisture content, and fuel loading. Fuel loading is the amount of combustible material that will be consumed in a fire under specific weather conditions for an area. Wildfires are more prominent in the western U.S., partly due to the higher levels of fuel loading. Estimated fuel loading data and emissions by region are shown in Table 3-2.

Table 3-2.
Estimated Fuel Loading and Emissions for Wildfires by Region[8]

Region	Average Fuel Loading (ton/acre)	Total Emissions (ton NO_X)
Rocky Mountain	37	57,300
Pacific	19	44,116
Southern	9	39,162
North Central/Eastern	11	5,119
Eastern	11	2,557

Because of numerous variables, estimating emissions is difficult. The topography of the land, along with the availability of fire-fighting personal and equipment, affects the land area burned by wildfires. The wind, ambient temperature, relative humidity, organically bound nitrogen and moisture in the fuel, and compaction of the fuel are all factors that affect NO_X emissions. However, the nitrogen content of the fuel is the most influential factor.[2] Fortunately, burning occurs at relatively low temperatures limiting the NO_X emissions. The formula used by EPA for estimating NO_X emissions resulting from wildfires is given in Equations 3-2 and 3-3.[8]

$$E_{NO_X} = F_{NO_X} A \qquad \text{Equation 3-2}$$

$$F_{NO_X} = P_{NO_X} L \qquad \text{Equation 3-3}$$

Where:

E_{NOx} = total NO_X emissions (lb NO_X)
F_{NOx} = emissions factor (lb NO_X /acre)
A = area of land burned (acres)
P_{NOx} = yield for NO_X (4 lb NO_X /ton of forest fuel)
L = fuel loading consumed (ton of forest fuel/acre)

Problem 3-1

The U.S. Forest Service reports that 7,000 hectares were burned in the southern region during the month of July. Estimate the NO_X emissions (in tons) for this region in July.

From Equation 3-3 and Table 3-2:

$$F_{NO_X} = P_{NO_X}\ L = \left(\frac{4\ \text{lb}\ NO_X}{\text{ton of forest fuel}}\right)\left(\frac{9\ \text{tons}}{\text{acre}}\right) = 36\,\frac{\text{lb}\ NO_X}{\text{acre}}$$

From Equation 3-2:

$$E_{NO_X} = F_{NO_X}\ A$$

$$= \left(\frac{36\ \text{lb}\ NO_X}{\text{acre}}\right)\left(\frac{\text{ton}}{2000\ \text{lb}}\right)(7{,}000\ \text{hectares})\left(\frac{2.47\ \text{acres}}{\text{hectare}}\right)$$

$$E_{NO_X} = 310\ \text{tons}\ NO_X$$

Prescribed burns serve as a means to reduce wildfire occurrences, remove logging debris, limit insect and disease problems, and promote natural new growth cycles. Because prescribed burns limit wildfires, they ultimately help reduce NO_X emissions from open burning.

3.2.2.4 Stratospheric Intrusion

Minimal amounts of NO_X are formed from stratospheric intrusion. Nitrous oxide in the stratosphere is oxidized and dissociated by solar radiation. The newly formed NO_X compounds descend to the troposphere.

3.2.2.5 Volcanoes and Geysers

Only trace amounts of NO_X and NO_3 are emitted from geogenic sources. Pollutants of concern for geogenic activity include particulate matter, sulfur dioxide, hydrogen sulfide, and carbon monoxide.

3.3 NO_X EMISSION TRENDS

The data provided in Table 3-3 provides some perspective in NOx emissions since the beginning of the twentieth century. These trends are due to the dramatically increased motor vehicle use and increased industrial capacity. After 1970, the impact of regulatory programs begins to become apparent. The NO_X emissions have been limited despite a substantial increase in use factors.

Table 3-3.
Percentage Change in National Emissions

Year	%
1900 to 1996	796
1940 to 1996	217
1970 to 1996	8
1987 to 1996	3
1990 to 1996	-2
1995 to 1996	-2

NO_X emissions in the U.S. from 1940 to 1998 (most recent data available) have been estimated based on emission inventory data and source population data.

Despite some uncertainties regarding the pre-1970 data, it is apparent that the NO_X emissions increased steadily from 1940 to 1970 (Figure 3-7). During this period of rapid industrial growth, the estimated NO_X emissions increased by 300%, from approximately 7 million tons per year in 1940 to more than 21 million tons in 1970.

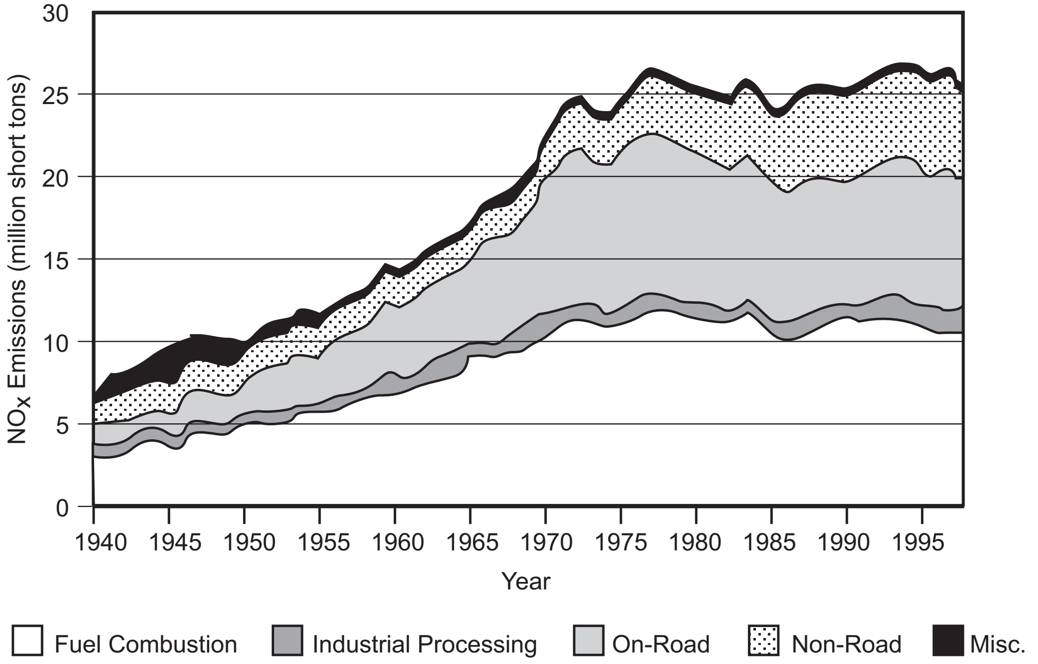


Figure 3-7. NO_x emission trends [1]

(The data in this updated graph is arranged differently than the graph shown on the broadcast video.)

After the enactment of the Clean Air Act Amendments of 1970 (CAAA 1970), NO_X controls imposed on both stationary and mobile sources have kept emissions at levels that are approximately equal to 1970, despite the continued increase in industrial activity and motor vehicle use since then.

Increased industrial activity and motor vehicle use is summarized in Figure 3-8. Considering that NO_X emissions have remained relatively stable, these trends suggest that the NO_X controls applied to motor vehicles and combustion sources have had some beneficial impact.

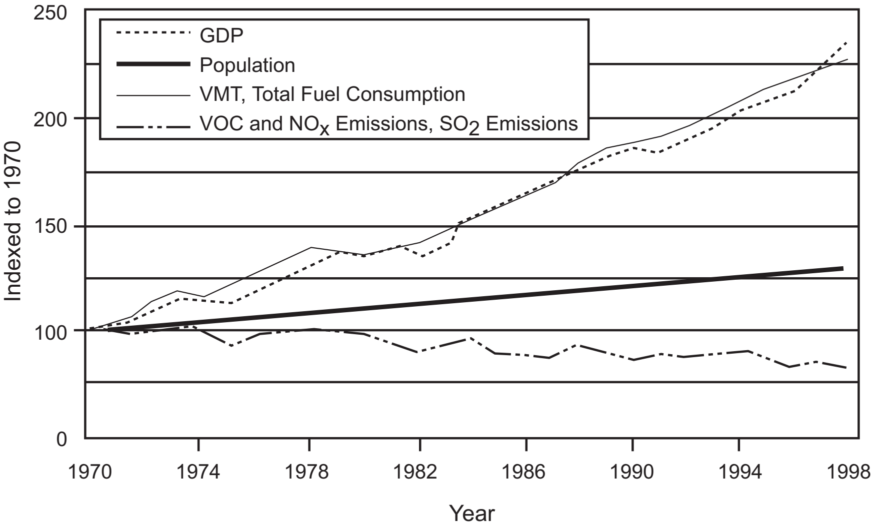


Figure 3-8. Trend of total NO_x emissions and related data, 1970-1998[1]

[Note: This updated graphic is slightly different than the graph used in the broadcast video.]

Despite improvements in motor vehicle emissions and stationary combustion source control, NO_X emissions have remained essentially at 1970 levels. This "unyielding" emissions profile is in contrast to the declining emission rates for other criteria air pollutants such as particulate matter, sulfur dioxide, carbon monoxide, and lead. Increased efforts to control NO_X are being stimulated by (1) the unyielding emission profile and (2) the important role of NO_X in the formation of ozone and other secondary pollutants.

3.4 OZONE SEASON EMISSIONS

Ozone season emissions data are important when discussing NO_X because NO_X is a precursor to the formation of ground-level ozone or smog. Smog occurs in the warmer months and can reach levels that are harmful to the public's health. Ozone formation is more prevalent in the warmer months because the summer meteorology is more conducive to ozone formation and also because summertime activities (e.g., higher electricity use due to air conditioning) produce more ozone precursor emissions such as NO_X. As a result of this seasonal variation, much of the NO_X modeling that is performed is done for the ozone season.

Ozone season emissions data are generated using two approaches. One approach is to collect activity data for a specific period of time (e.g., summer) and then use that data to develop the inventory for that period. The other more common approach is to develop an annual emissions inventory and then temporally allocate the annual emissions to the summer months. For example, one could examine the seasonal variation in production levels at an industrial facility and allocate annual emissions based on the seasonal variation in production levels. The main purpose of ozone season emissions data is to allow ozone modeling to be performed and also to allocate emission budgets for the NO_X SIP Call (discussed in Chapter 1).

3.5 EMISSIONS PROJECTIONS

As part of the NET, emissions are projected into the future to examine the effectiveness of regulatory programs on reducing NO_X emission levels and also to examine the impact of economic and demographic growth on NO_X emissions. Projections of the changes in activity patterns are based on activity data contained in various databases. These databases contain information on fuel use, economic indicators, population growth and product or services demand. Projections of the changes in emission levels are based on mandated emissions control programs, efficiency changes in emission generating activities, and the development of new technologies to reduce NO_X emissions.

Emissions projections are conducted every 3 years with the last projection conducted in 1997. Emissions are projected to the year 2010 at specified intervals.

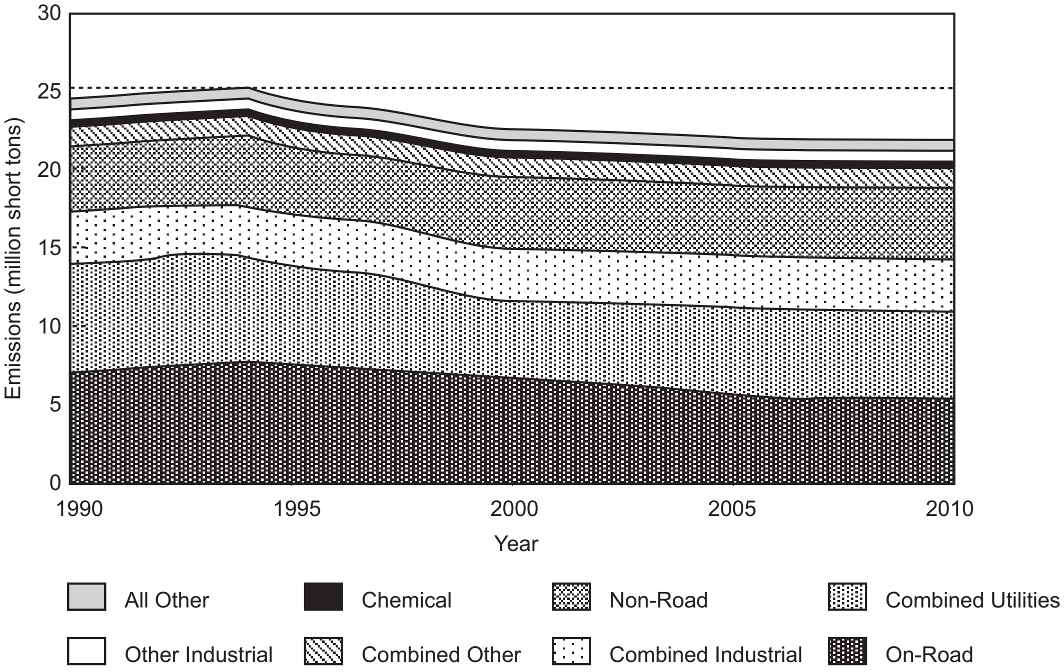


Figure 3-9. NO_X emissions projections

The NO_X emissions projections indicate that NO_X emission levels in the year 2010 will be reduced from mid-1990 levels by approximately 10% to 15%. This projected reduction is due to the impact of existing regulatory programs and does not include the benefits of newer NO_X regulatory control programs such as the NO_X SIP Call.

There are a variety of other sources of data concerning NO_X emissions. This other information is available from the EPA Emission Inventory Group and from the emission inventories compiled by the states. Air quality data from ambient monitoring networks also provide data of use in evaluating NO_X emissions. There are presently 224 NO_X ambient monitoring sites. These data might provide additional insight in the prevailing NO_X levels in specific areas.

Review Exercises

1. U.S. anthropogenic emissions of NO_X since 1970 have:
   a. Increased by 40%
   b. Increased by 20%
   c. Remained relatively constant
   d. Decreased 20%
   e. Decreased 40%

2. Which of the following is considered a non-road mobile source? (Select all that apply.)
   a. Simple cycle gas turbine
   b. Gasoline-powered lawn mower
   c. Diesel generator
   d. Nitric acid facility
   e. Front-end loader
   f. None of the above

3. NO_X emissions from EGUs are primarily generated by:
   a. Gas-fired boilers
   b. Oil-fired boilers
   c. Coal-fired boilers
   d. Wood-fired boilers
   e. None of the above

4. During which year were NO_X emissions the highest?
   a. 1940
   b. 1971
   c. 1977
   d. 1988
   e. 2000

5. During which year were highway mobile NO_X emissions the highest?
   a. 1940
   b. 1971
   c. 1978
   d. 1988
   e. 1993

References

---

[1] Environmental Protection Agency, Office of Air Quality Planning and Standards. December 1998. *National Air Quality and Emission Trends Report, 1997*. EPA 454/R-98-016. Research Triangle Park, NC.

[2] Environmental Protection Agency, Office of Air and Radiation. August 1997. *Nitrogen Oxides: Impacts on Public Health and the Environment.* Research Triangle Park, NC.

[3] Radian Corporation. May 1996. *Volume V: Biogenic Sources Preferred Methods-Final Report.* EPA-454/R-97-00. Research Triangle Park, NC.

[4] Environmental Protection Agency, Office of Air Quality Planning and Standards. March 2000. *National Air Pollution Emission Trends, 1900-1998.* EPA 454/R-00-002. Research Triangle Park, NC.

[5] Environmental Protection Agency, Office of Air Quality Planning and Standards. December 1997. *National Air Pollutant Emission Trends Report, 1900-1996*. EPA 454/R-97-011. Research Triangle Park, NC.

[6] Eastern Research Group, Inc. September 1996. *Report on Revisions to 5th Edition AP-42, Section 14.1 Soils.* Research Triangle Park, NC.

[7] Eastern Research Group, Inc. October 1996. *Report on Revisions to 5th Edition AP-42, Section 14.3 Lightening.* Research Triangle Park, NC.

[8] Environmental Protection Agency, Office of Air Quality Planning and Standards. *Compilation of Air Pollutant Emission Factors (AP-42), Section 13.1 Wildfires and Prescribed Burning.* 5th Edition. Research Triangle Park, NC.

4 NO_X Regulatory Programs

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Identify the impact of the Clean Air Act and its relationship to the EPA and the National Ambient Air Quality Standards.
2. Name the six criteria pollutants for which National Ambient Air Quality Standards have been established.
3. Explain the purpose of State Implementation Plans.
4. Describe the function of New Source Performance Standards and their relationship to industries.
5. Distinguish between pollutants covered by New Source Performance Standards and those covered by National Emission Standards for Hazardous Air Pollutants.

4 NO_X Regulatory Programs

4.1 INTRODUCTION

The purpose of this chapter is to review the national regulatory programs that serve as the basis for the regulation of NO_X emissions. This chapter will also review the scope of the NO_X control requirements and provide a basic level of understanding for the latter chapters of this manual.

Prior to discussing these regulatory programs that are driving the control of NO_X emissions, it is important to define some of the terms that will be used throughout the chapter.

National Ambient Air Quality Standards (NAAQS) are uniform, national standards concerning the levels of common air pollutants in the ambient air. They are promulgated to protect public health and welfare. These standards are expressed in terms of concentration (e.g., ppm or $\mu g/m^3$) with a corresponding averaging time (e.g., 1-hour, 8-hour, annual). In some cases, a NAAQS is promulgated with a specified number of allowable exceedances (e.g., a numerical value that cannot be exceeded more than once per year).

Beginning with the CAA of 1970, Congress charged EPA with the responsibility of establishing uniform NAAQS. These standards were set for a group of common air pollutants, which are emitted by numerous, diverse stationary and mobile sources. Primary standards for each pollutant were established at ambient levels considered necessary to protect public health. Secondary standards were established at more stringent levels for the protection of the public welfare (materials and crops).

By the end of 1990, EPA had identified the following six criteria pollutants and had promulgated NAAQS for them.

- Sulfur dioxide
- Nitrogen oxides
- Carbon monoxide
- Ozone
- Lead
- $PM_{2.5}$ and PM_{10}

These standards were based on comprehensive studies of available ambient monitoring data, health effects data, and material effects studies that were published as *Air Quality Criteria Documents*. The term *criteria pollutant* was derived from these regulatory support documents.

Following the 1970 CAA, each state was required to adopt and submit to EPA a plan providing for the implementation, maintenance, and enforcement of standards to attain and subsequently maintain the various NAAQS. These plans were called *State Implementation Plans* (SIPs).

Each of these plans included a detailed pollutant source emission inventory, dispersion modeling results, monitoring programs, a summary of the control strategy to be used for achieving the NAAQS in the required time, and a summary of the state's legal authority to administer and enforce the plan. Using its SIP, each state directed its own control regulations and approach toward its unique set of emission sources and circumstances. EPA reviewed these plans to confirm that they were reasonably designed to achieve the NAAQS.

If a SIP is not submitted, or if EPA deems the SIP to be inadequate to attain the NAAQS, the Federal government will promulgate a Federal Implementation Plan (FIP).

The 1990 CAAA have had a marked impact on the SIPs, requiring the states to modify their plans regarding the provisions affecting compliance with the ozone, particulate matter, and carbon monoxide standards. These three pollutants have proven to be especially difficult to control because of the variety of their potential urban sources and because of their photochemical precursors.

4.1.1 Clean Air Act Overview

The legal authority for regulating air emissions of NO_X is the Clean Air Act (CAA), often called *the Act*. This legislation modified and extended federal legal authority provided by the earlier CAAs of 1963 and 1970. The EPA was created on May 2, 1971 to implement the various requirements of the CAA of 1970.

Major amendments added to the CAA promulgated as the 1977 Clean Air Act Amendments (1977 CAAA). These amendments primarily concerned provisions for the Prevention of Significant Deterioration (PSD) of air quality in areas that attained the NAAQS. The 1977 CAAA also contained requirements pertaining to sources in non-attainment areas, which are geographic areas that do not meet one or more of the NAAQS. The 1977 CAAA established major permit review requirements to ensure attainment and maintenance of the NAAQS.

Another set of major amendments to the CAA occurred in 1990, substantially increasing the authority and responsibility of the federal government. New regulatory programs were authorized for control of acid deposition and for the issuance of stationary source operating permits. The National Emissions Standards for Hazardous Air Pollutants (NESHAPs) was incorporated into a greatly expanded program for controlling toxic air pollutants. In addition, the provisions for attainment and maintenance of NAAQS were substantially modified and expanded. Other revisions included provisions regarding stratospheric ozone protection, increased enforcement authority, and expanded research programs.

The 1990 CAAA now consists of the nine separate Titles listed in Table 4-1. Each of these Titles is subdivided into Parts, which are further subdivided into Sections. Some of the requirements that are most relevant to NO_X air pollution control are discussed in this chapter.

Table 4-1
Clean Air Act Organization

Title #		Description
Title I	-	Provisions for Attainment and Maintenance of National Ambient Air Quality Standards
Title II	-	Provisions Relating to Mobile Sources
Title III	-	Hazardous Air Pollutants
Title IV	-	Acid Deposition Control
Title V	-	Stationary Source Operating Permits
Title VI	-	Stratospheric Ozone and Global Climate Protection
Title VII	-	Provisions Relating to Enforcement
Title VIII	-	Miscellaneous Provisions
Title IX	-	Clean Air Research

4.2 NO_2 NAAQS

The numerical value of the NO_2 NAAQS is 100 $\mu g/m^3$ on an annual average basis. This standard is currently being attained in all areas of the country and, as such, does not currently serve as a forcing function for control of NO_X emissions.

4.3 OZONE NAAQS

Currently, two ozone NAAQS exist. The first was promulgated in 1977 and is a one-hour standard set at 0.12 ppm. It currently is applicable to those areas of the country that have not attained the standard.

The one-hour standard is based on the fourth-highest daily maximum one-hour average measured ozone level in a region over a three-year period. The one-hour standard will be phased out in other areas as they also come into attainment.

On July 17, 1997, EPA repromulgated the ozone NAAQS. This rulemaking established a new eight-hour average ozone limitation of 0.08 ppm.

Compliance with this standard is determined based on the fourth-highest daily maximum eight-hour average measured ozone level in a region over a three-year period. Areas throughout the east, south and midwest are expected to have ozone levels above this value. Certain metropolitan areas with limited natural dispersion (e.g., Los Angeles and Denver) are also expected to exceed the new eight-hour limit.

Designation of areas that are not attaining the new eight-hour standard was finalized on July 20, 2000.

A detailed discussion of the status of the ozone implementation strategies is presented in Section 4.7.

4.4 PM_{10} and $PM_{2.5}$ NAAQS

The particulate matter (PM) air quality standards represent another program that may impact the control of NO_X emissions to the atmosphere. Currently, there are two PM NAAQS: PM_{10} and $PM_{2,5}$. The PM_{10} NAAQS actually consists of two standards: a 24-hour standard that is in the form of a three-year average of the 99th percentile, not to exceed 150 $\mu g/m^3$, and an annual average not to exceed 50 $\mu g/m^3$. The $PM_{2.5}$ NAAQS also consists of two standards: a 24-hour standard, where the 98th percentile of the measured values cannot exceed 65 $\mu g/m^3$, and an annual average not to exceed 15 $\mu g/m^3$.

4.5 VISIBILITY IMPAIRMENT

The visibility impairment programs will require control of air emissions of NO_X. There are two types of visibility impairment programs: plume blight and regional haze. Plume blight is defined as a plume that can be traced to the source from which the plume originated. This type of visibility impairment is usually in the form of a straight-line plume or a layered plume, both of which obscure the vista. Regional haze is more widespread than plume blight and can extend in all directions over large land areas.

Both plume blight and regional haze can be caused by fine particulate matter and NO_X in the atmosphere. NO_X can cause a brownish plume. The reduction in visibility is related to the formation of PM_{10} and smog-generated aerosols.

As part of the 1977 CAA amendments, Congress established a goal of remedying any existing visibility impairment and preventing future visibility impairment in mandatory Class I areas. Class I areas include National Parks and Wilderness Areas. EPA issued regulations to address plume blight in 1980 and promulgated regulations to address the Regional Haze issue on July 1, 1999.

With respect to the development of regulations for Regional Haze, EPA is encouraging all 48 contiguous states to begin working cooperatively to control regional haze. This work is likely to include (1) determining the regions of the country that are likely to be affected by regional haze, and (2) developing SIPs to protect the 156 designated Class I areas, such as national parks.

The reduction in visibility is related to the formation of PM_{10} particulate matter and smog-generated aerosols. Accordingly, the regional haze rulemaking is highly interrelated to the NO_X SIP Call, the Ozone NAAQS, the Section 126 Petitions and the PM_{10} NAAQS. Actions taken with respect to one or more of these regulatory programs will also benefit regional haze. Figure 4-1 shows the concentration of regional haze across the U.S.

Visibility Impairment in Deciviews (DV)

IMPROVE Data 1992 - 1995

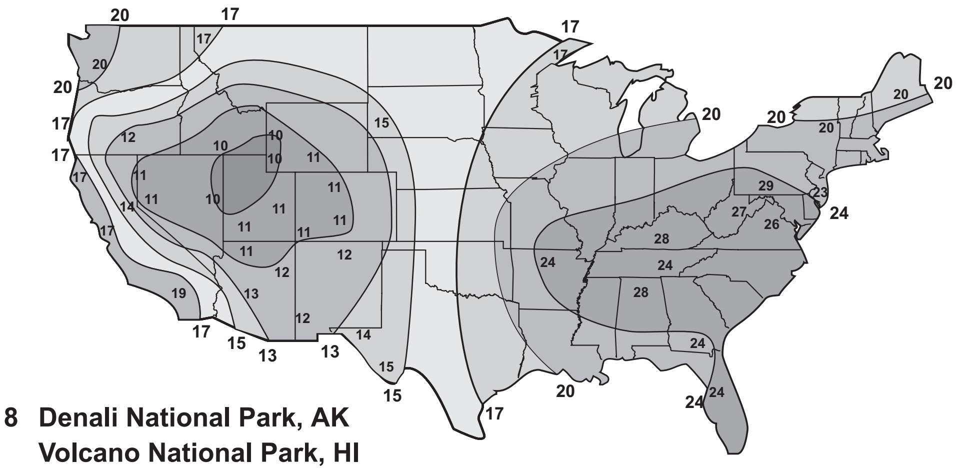


Figure 4-1. Regional haze across the U.S.

The *Regional Haze Guidance* is a regulatory program directly aimed at curbing NO_X emissions of stationary sources. The *Regional Haze Guidance* originated after the President issued a memorandum to EPA on July 16, 1997 concerning the implementation of the revised air quality standard for ozone and particulate matter. The final guidance document, *Emission Inventory Guidance for Implementation of Ozone and*

Particulate Matter National Ambient Air Quality Standards and Regional Haze Regulations, was issued on May 13, 1999. The U.S. Circuit Court of Appeals for the District of Columbia issued a ruling on May 14, 1999 remanding the ozone and particulate matter standards. However, EPA believes the majority of the guidance will not be affected by the Court's final decision.[1]

The pollutants targeted within the guidance include all precursors to ozone and regional haze, with NO_X being a major contributor to both ozone and regional haze. The guidance also sets new definitions for Class I and *non-attainment* areas for all states. EPA is phasing out the one-hour ozone standard as it moves to implement the eight-hour ozone standard in order to address longer exposure times.

EPA repealed the one-hour standard for most areas in June and July of 1998. The cancelled one-hour standard was based on EPA's air quality data showing that areas were attaining the one-hour ozone standard of 0.12 ppm. EPA will continue to cancel the one-hour standard on an area-by-area basis and will, instead, place these areas under the new eight-hour standard.

In the proposed guidance plan EPA states that "With greater understanding of the regional nature of ozone, the recent recommendations of OTAG now focus on reducing nitrogen oxide emissions from large power plants and industrial boilers, many of which are located in attainment areas but which have been found to contribute to non-attainment area problems."[2]

Because of the required three-year monitoring period under the Regional Haze Program, areas must implement the controls required for compliance three years prior to the actual attainment date. EPA is to designate areas either as attainment or non-attainment for ozone and PM_{10} by July 2000. Within three years of being determined to be a non-attainment area, that area must submit a SIP.

4.6 HISTORIC REVIEW OF OZONE CONTROL STRATEGIES

The most important program in the control of NO_X emissions has been the program designed to control ozone. Historically, the focus of the ozone control program has been the control of volatile organic compounds (VOCs), mostly in urban or metropolitan areas. In 1991, the National Academy of Science (NAS) issued a report that recommended that EPA focus more on the control of NO_X to attain the ozone NAAQS. The CAAA of 1990 included a provision for the establishment of the Ozone Transport Commission (OTC). The OTC is concerned with the northeastern states located between Northern Virginia and Maine.

As a result of the OTC, EPA and the state and local air pollution control agencies have developed ozone control requirements that apply over broad geographic areas. Four programs that require additional NO_X controls to attain the ozone NAAQS are the one-hour Ozone NAAQS, the NO_X SIP Call, Section 126 Petitions, and the eight-hour Ozone NAAQS. Each of these programs is discussed in the following subsections.

4.6.1 One-Hour Ozone NAAQS

Non-attainment areas still under the one-hour ozone standard were scheduled to be officially categorized on July 20, 2000 as *extreme*, *serious-17*, *serious-15*, *moderate*, or *marginal* (65 FR 45181). These non-attainment areas must implement plans to meet both the one-hour and the eight-hour standards. These non-attainment areas are shown in Figure 4-2.

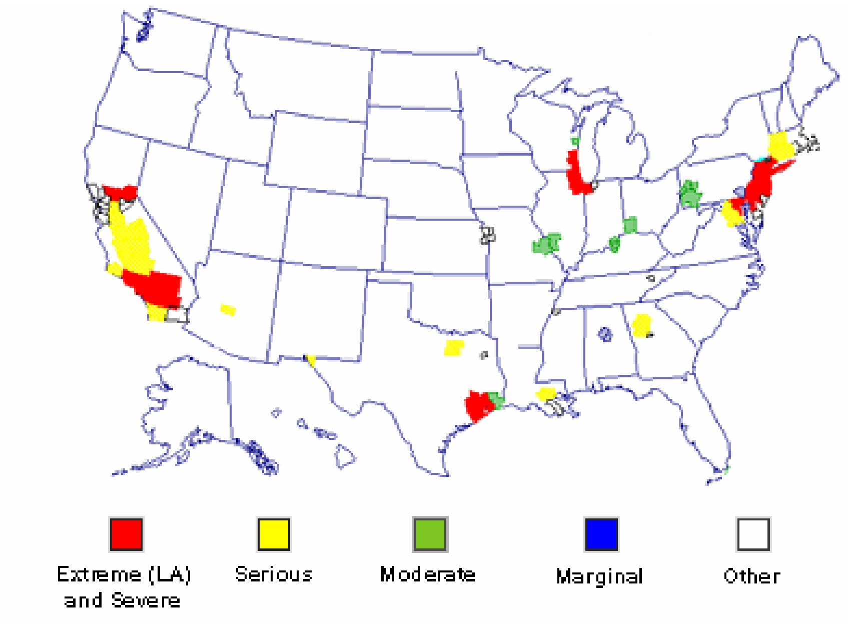


Figure 4-2. Non-attainment areas under the one-hour ozone standard

As a result of the OTC work and the development of SIPs to meet the one-hour ozone standards, many state and local air pollution control agencies found that control of pollutants being transported into the state is necessary to achieve the ozone NAAQS. Therefore, in 1995 EPA and 37 states formed the Ozone Transport Assessment Group (OTAG) to address the issue of ozone regional transport. OTAG conducted a two-year study of ozone transport and recommended that additional NO_X controls are needed to attain the ozone NAAQS.

4.6.2 NO_X SIP Call

Based on the OTAG recommendations, dispersion modeling and public comments, EPA published a NO_X SIP Call requiring states to revise their SIPs to include additional control on NO_X emissions in order to demonstrate attainment of the ozone NAAQS. This rule was promulgated on October 27, 1998 and requires 22 states and the District of Columbia to meet a NO_X budget by May 1, 2003.

> The purpose of the NO_X SIP Call is to reduce the amount of ground level ozone formed during regional transport of air masses by limiting NO_X emissions.

Additional information on the NO_X SIP Call can be obtained at the web address *http://www.epa.gov/airlinks*.

The final ruling on the Regional NO_X Emission Reduction (NO_X SIP Call) identifies the 22 states, shown in Figure 4-3, that contribute significantly to ozone problems in downwind areas.

> After the issue of the NO_X SIP Call, several parties challenged EPA in court. On March 3, 2000, the United States Court of Appeals for the District of Columbia Circuit issued a decision to uphold the NO_X SIP Call in all states except Wisconsin, western Missouri and southern Georgia.
>
> These states must develop strict NO_X control requirements applicable to stationary sources in order to minimize ozone emissions during the summertime ozone season. The ozone season varies from state to state, but is generally defined as May 1 through September 30 in the northern hemisphere. The photochemical reactions causing ozone formation are most effective during this time period because of high solar irradiation rates and high ambient temperatures.

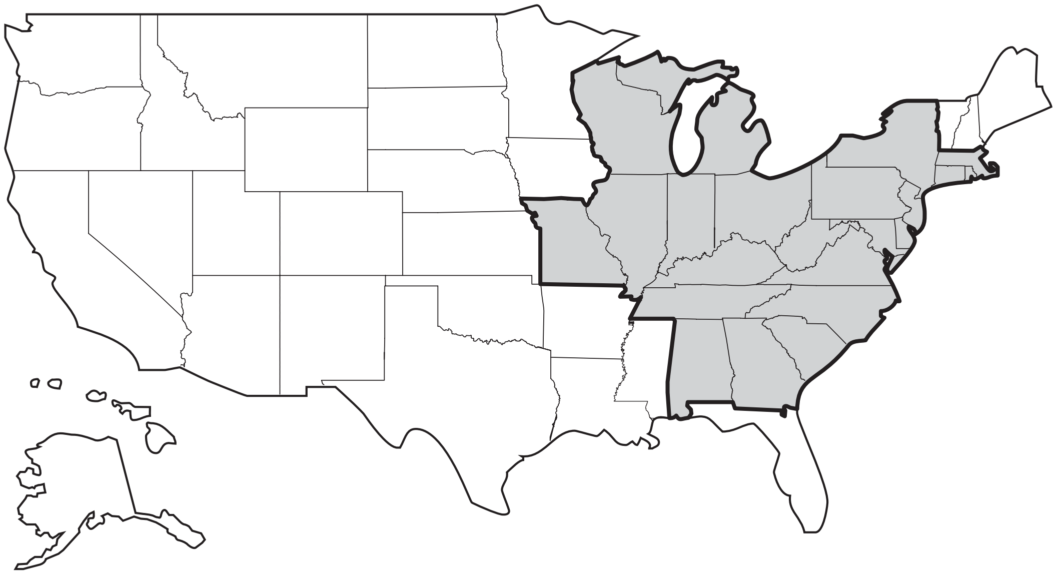


Figure 4-3. States and territories originally subject to the NO_x SIP Call

The NO_X SIP Call requires the affected states to prepare and submit a revised SIP to EPA that addresses how they will reduce the transport of NO_X emissions across state boundaries. Each individual state has the freedom to meet the requirements of the SIP rule by reducing emissions from the sources they choose. However, to ensure that the SIPs are effective in achieving their goal, EPA has published a proposed Federal Implementation Plan (FIP). The proposed FIP would be imposed on a state that failed to submit a SIP to EPA or submitted an inadequate SIP. The FIP was published on October 21, 1998 and is consistent with the NO_X SIP Call. Additional information on the FIP can be obtained at the web address *http://www.epa.gov/airlinks.*

4.6.3 Section 126 Petitions

Section 126 of the CAA empowers any state with authority to petition for EPA to set emissions limits for specific sources of pollution in other states that significantly contribute to its air quality problems. In August 1997, eleven northeastern states (Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, and Vermont) and the District of Columbia filed petitions seeking to reduce the amount of ozone transported into their state boundaries under CAA Section 126. These states requested that EPA make a finding that NO_X emissions from certain stationary sources in other states significantly contribute to their ozone non-attainment problems.

On October 21, 1998 EPA published a proposal in response to the Section 126 petition that was consistent with the NO_X SIP Call. More information on the Section 126 petition can be obtained at the web site previously mentioned in Section 4.6.2 of this manual.

In December 1999, EPA made a final rule on eight of the eleven petitioning states. The petitions from Connecticut, Massachusetts, New York, and Pennsylvania were granted. 392 EGU and non-EGU facilities were targeted in 12 states (Delaware, Indiana, Kentucky, Maryland, Michigan, North Carolina, New Jersey, New York, Ohio, Pennsylvania, Virginia, and West Virginia) and the District of Columbia. These facilities must implement controls or use emission allowances through the federal cap-and-trade program by May 1, 2003.[3]

4.6.4 Eight-Hour Ozone NAAQS

The new eight-hour standard is expected to result in non-attainment areas that are spread over large geographic areas in the eastern U.S.

The new eight-hour NAAQS is now in effect throughout the U.S. The areas that are not yet in attainment retain the one-hour standard. Areas that attain the eight-hour 0.08-ppm limit will be categorized as attainment areas. If an area demonstrates that it can attain the eight-hour standard with the control measures in its SIP, then the EPA will consider that the area has met the CAA requirements for reasonable available control measures, and additional measures will not be required.

Areas not meeting the eight-hour attainment status (non-attainment areas) will be categorized as *transitional*, *traditional*, or *international transport*. Designation of non-attainment eight-hour areas was finalized on July 20, 2000.

The transitional status will concern most of the 21-state region and District of Columbia covered under the NO_X SIP Call.

For these areas few, if any, additional control measures beyond those covered under the NO_X SIP Call will be required. States are required to submit SIP revisions by May 2000 for areas classified as transitional. The control requirements contained in those revised SIPs must be implemented by May 2003, and the new eight-hour ozone NAAQS must be attained by December 2005.

Areas that do not fall under the transitional or international transport classification will be considered traditional. Traditional areas are those that are not attaining the one-hour ozone standard. States are required to submit SIP revisions by July 2003 for areas classified as traditional. The control requirements contained in those revised SIPs must be implemented between 2005 and 2008, depending on the classification of the area for the one-hour ozone NAAQS. The new eight-hour ozone NAAQS must be attained in traditional areas between 2007 and 2010.

Areas that cannot attain the eight-hour ozone NAAQS due to emissions from another country will be placed under international transport status. States are required to submit SIP revisions for areas classified as transitional by July 2003. The control requirements contained in those revised SIPs must be implemented by 2005 and the new 8-hour ozone NAAQS must be attained by December 2007.

4.7 ACID RAIN

As discussed in previous chapters, the detrimental environmental effects associated with exposure to NO_X provide the basis for the control of NO_X. These impacts include acid deposition, water body eutrophication (i.e., reduction of oxygen content), fine particle formation, and degradation of visibility. In addition, NO_X reacts in the presence of sunlight to form tropospheric ozone, which has been associated with environmental impacts.

The Title IV NO_X reduction program is mandated by the CAAA of 1990 and is designed to reduce acid deposition through the reduction in emissions of SO_2 and NO_X from utilities. It is important to note that the Title IV NO_X reduction program only applies to coal-fired electric utilities. The program also supports the Title I requirements to reduce tropospheric ozone and incorporates a flexible compliance framework (to be discussed later in this chapter).

The Title IV NO_X reduction program affects boilers and categorizes them as Group 1 or Group 2. Group 1 boilers include dry bottom wall-fired and tangentially-fired boilers. Group 2 boilers include cyclones, cell burners, wet bottom boilers, vertically fired boilers, and all other boilers (stokers and fluidized beds).

> Under Title IV, acid rain reduction is to be accomplished through a two-phased program that uses energy conservation, clean coal technology, and the cap and trade program.

Phase I affects Group 1 boilers and extended from January 1, 1996 through December 21, 1999. Phase II affects Group 2 boilers and any Group 1 boilers that were not included in Phase 1. Phase II began on January 1, 2000.

Phase I

The regulations for the Phase I program were promulgated on April 13, 1995 and applied to some Group 1 boilers. As of 1997, 265 Group 1 boilers were subject to the Phase I program. The rule identified NO_X emission limits that apply to the Group 1 boilers. These include 0.50 lb NO_X/MMBtu for dry bottom, wall-fired boilers and 0.45 lb NO_X/MMBtu for tangentially-fired boilers.

The regulations provide affected sources with a number of compliance options. The first option is to comply with the emission limits listed above. Another option allows affected facilities to average emissions across two or more boilers, such that the average emission rate across the boilers complies with the stated emission limits. Finally, the sources can also petition EPA for an alternative emission limit (AEL). An AEL is appropriate in those cases where a control technology designed to meet the emission limit is installed and is operated in accordance with the manufacturer's recommendation, yet the emission limit is not achieved. In this case, the affected facility may petition EPA for an AEL. EPA will evaluate and rule on each request for an AEL on a case-by-case basis.

EPA has estimated the annual impacts associated with Phase I of the Title IV NO_X reduction program to be 1.17 million tons of NO_X reduction at a cost of $267 million. This translates to a cost-effectiveness of $227/ton of NO_X reduced.

Phase II

Regulations for the Phase II program were promulgated on December 19, 1996 and applied to 607 boilers in Group 1 and 145 boilers in Group 2. The rule identified NO_X emission limits for Groups 1 and 2. Group 1 boiler emission limits are 0.46 lb NO_X/MMBtu for dry bottom, wall-fired boilers and 0.40 lb NO_X/MMBtu for tangentially-fired boilers. It should be noted that these limits are more stringent than Group 1 limits under Phase I. Group 2 emission limits are 0.68 lb NO_X/MMBtu for cell burners; 0.86 lb NO_X/MMBtu for cyclones greater than 155 megawatts of generating capacity; 0.84 lb NO_X/MMBtu for wet bottom boilers greater than 65 megawatts of generating capacity; and 0.80 lb NO_X/MMBtu for vertically-fired boilers.

As with Phase I, Phase II regulations provide affected sources with a number of compliance options. In addition to the three options that were available under Phase I, Phase II provides an additional compliance option. Specifically, Phase II Group 1 boilers could have elected to comply with the less stringent Phase I Group 1 standard, provided that their compliance with the less stringent standard was achieved by January 1, 1997. For example, a dry bottom, wall-fired boiler under Phase II is required to comply with a NO_X emission limit of 0.46 lb/MMBtu. Instead, the facility operating this boiler could have elected to comply with the Phase I limit for dry bottom, wall-fired boilers of 0.50 lb NO_X/MMBtu by January 1, 1997. Election of this compliance option would have grandfathered the boiler from complying with the more stringent Phase II limits until 2008. This early election compliance option provides sources with certainty in planning compliance strategies on a long-term basis while encouraging early reduction of NO_X emissions.

EPA has estimated the annual impacts associated with Phase II of the Title IV NO_X reduction program to be 890,000 tons of NO_X reduction at a cost of approximately $200 million. This translates to a cost-effectiveness of $229/ton of NO_X reduced.

Owners or operators of stationary sources subject to these new regulations are required to install on each unit CEMS for sulfur dioxide, nitrogen oxides, volumetric flue gas flow, and opacity. These instruments will be the primary sources of information for calculating the total pollutant emission rates. Alternative emission calculation procedures based on general plant operating parameters must be used when CEMS data are unavailable. The emission data must be reported to EPA on a regular basis. Enforcement personnel will review this data to confirm that emissions are less than the allotment for that specific facility.

Excess emission penalties will be assessed if any source exceeds the yearly emission limitation. Furthermore, sources will be required to offset the excess emissions by an equal tonnage amount in the subsequent year. Enforcement personnel will have an important role in evaluating the adequacy of the emissions data, determining the need for penalties, and confirming that excess emission offsets have been achieved.

In summary, in 1995 approximately 6.09 million tons of NO_X were emitted from boilers affected by the Title IV program. The Phase I program has implemented a 34% reduction of this total, a reduction of 2.06 million tons. Additional information on the Title IV NO_X reduction program can be found at the web address *http://www.epa.gov/acidrain*.

4.8 OTHER PROGRAMS

As stated in Chapter 1, recent rulemakings designed for ozone attainment have been aimed at minimizing NO_X emissions rather than VOC emissions to control ozone, the NO_X SIP Call and the Regional Haze Program being examples. However, other regulatory programs that target the control of NO_X emissions include New Source Review (NSR), Prevention of Significant Deterioration (PSD), Cap and Trade, and the New Source Performance Standards (NSPS). All these programs serve as regulatory “drivers” for sources requiring NO_X control equipment, and each of these is discussed in the following subsections.

4.8.1 New Source Review

The New Source Review (NSR) program, which was established by the 1977 CAAA, requires all major new sources or substantially modified sources (including sources of NO_X) in both non-attainment areas and attainment areas to obtain permits. NSR permits are determined on a case-by-case basis by one of the 10 EPA regional offices. Permitting application guidelines for attainment areas are covered by the Prevention of Significant Deterioration (PSD) program. NSR and PSD programs cover NO_X and other criteria pollutants.

Permitting of major new sources in non-attainment areas is more time consuming and complicated than PSD permitting requirements because of the numerous requirements in the CAA that apply directly to major sources in non-attainment areas. To obtain a permit under the NSR program a facility must install control equipment that complies with the Lowest Achievable Emission Rate (LAER) and demonstrate an offset of current pollutant emissions.

The LAER is defined as the more stringent of the following limitations:

- The most stringent emission limitation contained in a SIP of any state for the same class or category of source (unless it is demonstrated that this limitation is unachievable).
- The most stringent emission limitation achieved in practice.

Economic costs are not a consideration in determining LAER control technology.

4.8.2 Prevention of Significant Deterioration

Prior to the 1977 CAAA, the NAAQS only protected non-attainment areas. Virtually no restrictions were placed on facilities located in attainment areas. The PSD program was introduced within the NSR program to address this issue. The basic purpose of the PSD program is to maintain the air quality of the most pristine areas of the country and to allow a specified pollutant increase in other areas. A facility covered by the PSD program must take into account the level of air quality already attained in that area.

The PSD program is aimed at protecting Class I areas. Class I areas include national parks, national wilderness areas, national monuments, national seashores, and other areas of special national or regional natural, recreational, scenic, or historic value. Essentially no degradation of Class I areas is allowed under the PSD program. A decrease of emissions from an existing facility in a Class I area may be necessary for the permitting of a new facility. Existing major sources, modified existing minor sources, and new plants considered major sources and which contribute to the deterioration of air quality in Class I areas are subject to the program and must apply for a permit.

The PSD permitting process is extensive and can be lengthy in duration. In order to obtain a permit a source must do the following:

1. Evaluate the Best Available Control Technology (BACT). BACT is based on the most stringent control available for a similar source category that is technically and economically feasible.
2. Perform an ambient air impact study.
3. Conduct additional impact studies including visibility, soils, and vegetation.

Class II areas include all attainment areas and all unclassified areas that are not classified as either Class I or as industrialized attainment areas. A restricted increase over baseline levels is allowed in these areas. Industrialized attainment areas are classified as Class III and have less stringent allowable increases in emissions than Class I and Class II areas.

4.8.3 Cap and Trade Program

EPA has established incentives for companies through the Cap and Trade program. The Cap and Trade system rewards facilities by allowing them to sell their excess emission reductions to other facilities that require assistance in reducing emissions. In order to sell their emissions credits, facilities must either reduce their emissions before the deadline or achieve emission levels lower than required. The goal of the program is to allow companies to determine the most cost-effective method of meeting emission standards.

A Cap and Trade program is established for the Ozone Transport Commission (OTC) NO_X emission trading program, the NO_X SIP Call, and for SO_2 trading by utility companies operating boilers subject to the 1990 CAAA Title IV acid rain requirements. EPA is encouraging, but not requiring, states affected by the NO_X SIP Call to participate in the NO_X emissions Cap and Trade program. EPA has included incentives to sources that achieve early reductions of NO_X from the 1999 ozone season through the 2002 ozone season. These emission reductions can be banked and used with certain restrictions during future ozone seasons.

For a facility to be eligible for emission trading, the emission reductions must go beyond regulatory requirements imposed by the Title IV acid rain (Phase II) requirements, the NO_X SIP Call emission limits, and other related emission limitations. Emission reductions must be quantifiable using CEM systems meeting 40 CFR Part 75 of the Acid Rain Program requirements. Emission reductions must be verifiable through the use of adequate records and reports.

Within these limits, EPA proposes to permit the widest possible flexibility in emission trading and banking. Accordingly, it appears that sources will be allowed to trade emission allowances across state lines within a small number of zones. Furthermore, it should be possible to trade allowances between different classes of industrial sources included in the scope of the NO_X SIP Call (i.e., from utility boilers to industrial boilers, or from cement kilns to gas turbines).

EPA has established a pool of credits to help ensure that the availability of electricity will not become a problem. States may issue credits if sources achieve their reduced emission levels before the deadline or if sources demonstrate a need for relief because they are not able to meet the compliance deadline.

4.8.4 New Source Performance Standards

NSPS originated with the CAA of 1970. The authority for the NSPS regulations is in Section 111 and covered by Title V. NSPS regulations establish stringent emission limitations for new or substantially modified sources in designated industrial categories regardless of the state or ambient air quality region in which the source is located. These source category limits are the maximum allowable emissions for the applicable sources. The emission limits are meant to represent the “best demonstrated technology,” taking into consideration cost and energy and environmental impacts. The basis for NSPS limits is different than for BACT. NSPS levels are negotiated as industry-wide standards, while BACT is determined on a case-by-case basis. For this reason, BACT standards are usually more stringent than NSPS standards.

The source categories affected by NSPS regulations are those that have been identified by EPA as emitting one or more pollutants in quantities significant enough to endanger the public health or welfare. Under the NSPS regulations these sources must either (1) achieve the degree of emission limitation or percentage reduction or (2) apply a design, equipment, work practice, operational standard, or combination which reflects the best available technological system of continuous emission reductions. Examples of general control methods currently in use under the NSPS regulations include the following:

- Air pollution control systems such as electrostatic precipitators, fabric filters, wet scrubbers, and dry scrubbers
- Precombustion cleaning or treatment of fuels
- Inherently low-polluting or nonpolluting production processes
- Work practices and operational standards

Between 1970 and 1990, the U.S. EPA promulgated NSPS standards for more than 70 source categories. The owner/operator of a new or modified source subject to one of the NSPS regulations must demonstrate compliance within 180 days of initial start-up of the facility and at other times as required by EPA. Primary authority for the enforcement of these regulations rests with EPA. However, in most cases, this authority has also been delegated to the states. In such cases, the states and EPA have concurrent enforcement authority.

NSPS standards cover the same facilities regulated by the PSD and NSR programs. However, these programs differ in a few important aspects. One difference is that NSPS is the responsibility of the federal EPA, while NSR/PSD is the responsibility of one of the 10 EPA regional offices. In addition, NSPS sets an emission limit standard covering all facilities included in a specified source category; while NSR/PSD emission limits are established on a case-by-case basis.

Revised Fossil Fuel-Fired Boilers NSPS

On September 24, 1998, EPA repromulgated the NSPS NO_X limits for utility boilers (40 CFR Part 60, Subpart Da) and industrial boilers (40 CFR Part 60, Subpart Db). The reductions were made to reflect the performance of the most recent best demonstrated technology. After considering available performance data and performing cost analyses, EPA chose Selective Catalytic Reduction (SCR) as the basis for revising the NO_X emission limits for both categories of boilers.

In the revised NSPS, EPA states that, “The revisions being promulgated reflect the Administrator’s determination that the best system of NO_X emission reduction (taking into consideration the cost of achieving such emission reduction and non-air quality health and environmental impact) for these sources is now reflective of flue gas treatment technologies, particularly SCR.”[4] The new limits are based on coal-firing electric utility boilers and industrial boilers with SCR units installed in combination with combustion controls.

The new revisions regulate NO_X, SO_2, and PM emissions by developing a single limit for an industrial category. The limit is expressed as emissions per unit of output energy. The new emission limits are on a “fuel neutral emission rate,” which is meant to add flexibility and encourage industry to use cleaner fuels such as natural gas.

The NSPS revisions affect those utility and industrial boilers for which construction is commenced after the date of proposal. The EPA estimates that 17 new utility boilers and 381 new industrial boilers will be constructed in the next five years.

The new limits would reduce NO_X emissions by approximately 42% from the existing standards. The reduction of baseline NO_X emissions from utility steam generating units is approximately 23,000 Mg/year (25,800 tons/year) and from industrial steam generating units is 18,000 Mg/year (20,000 tons/year) in the fifth year after proposal.[4]

Subpart Da of the NSPS covers electric utility steam generating units that are capable of combusting more than 73 MW (250 MMBtu/hr) heat input of fossil fuel. The NO_X emission limit in the final rule for newly constructed subpart Da units is 200 ng/J_O [1.6 lb/megawatt-hour (MWh)] gross energy output, regardless of fuel type. The NO_x emission limit in the final rule for existing sources that become subject to subpart Da through modification or reconstruction is 65-ng/J_I [0.15 lb/MMBtu] heat input.

Industrial-commercial-institutional steam generating units greater than 29 MW (100 MMBtu/hr) of power are categorized under Subpart Db. For units covered under subpart Db, the NO_X emission limit being promulgated is 87 ng/J_I (0.20 lb/MMBtu) heat input from the combustion of natural gas, oil, coal or a mixture containing any of the fossil fuels. However, for low heat release rate units firing natural gas or distillate oil, the current NO_X emission limit of 43 ng/ J_I (0.10 lb/MMBtu) heat input is unchanged.

Review Exercises

1. Which of the following programs are designed to attain the ozone NAAQS through the control of NO_X emissions?
   (Select all that apply.)
   a. Eight-hour ozone NAAQS
   b. NO_X SIP Call
   c. Section 126 Petitions
   d. One-hour ozone NAAQS
   e. All of the above

2. Which of the following distinguishes pollutants covered by NAAQS from those covered by NESHAPs?
   (Hint: Choose the answer associated with those pollutants covered by NAAQS.)
   a. These pollutants are only emitted by fossil fuel-fired boilers.
   b. Causes irreversible or incapacitating illness at low concentrations.
   c. Emitted by numerous diverse stationary and mobile sources.
   d. All of the above

3. Match the following acronyms with the descriptions given.

   a. SIP
   b. NAAQS
   c. NSPS
   d. PSD

   i. Stringent emission limitations for new or substantially modified sources in designated industrial categories regardless of the state or ambient air quality region in which the source is located.
   ii. Standards set for the group of six common air pollutants (criteria pollutants) defined by EPA. The standards are to maintain low concentrations of the criteria pollutants in the ambient air in order to protect public health.
   iii. Plan developed by state air pollution control agencies to demonstrate attainment of the NAAQS.
   iv. Regulation aimed at protecting Class I and other attainment areas.

4. Match the following acronyms with the descriptions given.

   a. BACT
   b. NSR
   c. SIP
   d. LAER

   i. Case-by-case emission limits based on the most up-to-date methods, systems, techniques, and production processes available to achieve the greatest feasible reductions taking into consideration energy, environmental, and economic impacts.
   ii. A state plan adopted and submitted to EPA that addresses the implementation, maintenance, and enforcement of standards set forth by EPA.
   iii. Requires all major new sources and significantly modified sources in both non-attainment areas and attainment areas to obtain permits.
   iv. The best and most up-to-date control technology without consideration of economic cost used to determine emission limits for the NSR program.

5. When were the NAAQS first introduced into law?
   a. 1963
   b. 1967
   c. 1970
   d. 1990

6. When was acid deposition control under Title IV first promulgated?
   a. 1963
   b. 1967
   c. 1970
   d. 1990

7. Title IV requires the reduction of which of the following emissions? (Select all that apply.)
   a. Sulfur dioxide
   b. Ozone
   c. Nitrogen oxides
   d. None of the above

References

---

[1] Mobley, J. D. July 2, 1999. *Memorandum - Implications of the Court Decision on Emission Inventory Guidance.*

[2] Environmental Protection Agency, Office of Air Quality Planning and Standards. November 18, 1998*. Emission Inventory Guidance for Implementation of Ozone and Particulate Matter National Ambient Air Quality Standards (NAAQS) and Regional Haze Regulations– Draft Guidance.* Research Triangle Park, NC.

[3] Environmental Protection Agency. *Findings of Significant Contributions and Rulemaking on Section 126 Petitions for Purposes of Reducing Interstate Ozone Transport*. 40 CFR Parts 52 and 97.

[4] Environmental Protection Agency. *Revision of Standards of Performance for Nitrogen Oxide Emissions From New Fossil-Fuel Fired Steam Generating Units; Revisions to Reporting Requirements for Standards of Performance for New Fossil-Fuel Fired Steam Generating Units.* RIN-2060-AE56, Final Rule. 40 CFR Part 60.

5 Combustion Sources

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Identify the three major types of combustion sources.
2. Name the main types of boilers and explain their basic operation.
3. Distinguish among the three main types of pulverized coal-fired boilers.
4. Identify the major components of boilers and their roles in the combustion process.
5. Explain the basic features of the two types of internal combustion engines.
6. Describe the basic operation of a municipal waste incinerator.

5 Combustion Sources

Based on the emission inventory presented in Chapter 3, utility and industrial boilers, gas turbines, and stationary internal combustion engines are very important sources of NO_X.

This chapter provides fundamental information concerning these combustion sources and introduces terms used throughout the course. This information will facilitate later discussions concerning (1) combustion modifications to suppress formation, and (2) add-on control techniques to reduce NO_X emissions formed in combustion sources. It should be noted that add-on control techniques are also termed *post-combustion control systems.*

Section 5.1 discusses pulverized coal-fired boilers, cyclone-fired boilers, spreader stoker boilers, fluidized bed boilers, and gas- and oil-fired boilers. Section 5.2 concerns reciprocating and rotary stationary internal combustion engines. Section 5.3 examines municipal waste incinerators.

It is important to understand the basic characteristics of combustion processes because these systems must be modified to minimize NO_X formation. Combustion processes have historically been designed to (1) maximize fuel economy, (2) minimize carbon monoxide and partially oxidized organic compound emissions, and (3) minimize furnace volume requirements. This has been accomplished by rapid and complete fuel-air mixing and allowing adequate time for oxidation. The procedures necessary to control NO_X can be in conflict with these normal design practices. Specifically, it is often necessary to (1) minimize peak gas stream temperatures, (2) minimize the quantity of oxygen available, (3) minimize the mixing rates of fuel and air, and (4) maximize as much furnace as possible for combustion. The next several chapters focus on balancing conditions required for adequate combustion with conditions required for minimizing NO_X.

5.1 BOILERS

5.1.1 General Characteristics

Figure 5-1 presents a very basic view of a boiler, where the boiler is represented by the combustion zone.

> Boilers are supplied fuel at a rate that is based on the demand for steam. The steam could be used to generate electrical power in a turbine, as a source of energy for powering equipment, or for space heating. Combustion air is supplied at a rate necessary to maintain a pre-set air-fuel ratio. When the boiler is operating near its maximum rated load, the quantity of air needed per unit mass of fuel is relatively low. When the boiler is operating at mid or low load, the quantity of air needed per unit mass of fuel increases slightly. The air-fuel ratio is changed because of the less favorable combustion conditions that exist at the mid and low loads.

Air and fuel are introduced into the boiler and combusted to form CO_2 and H_2O gases that are exhausted from the combustion zone. The combustion controller component is often called the *boiler master* in commercial boilers. The necessary air-fuel ratio is determined automatically for essentially all boilers by the combustion controller.

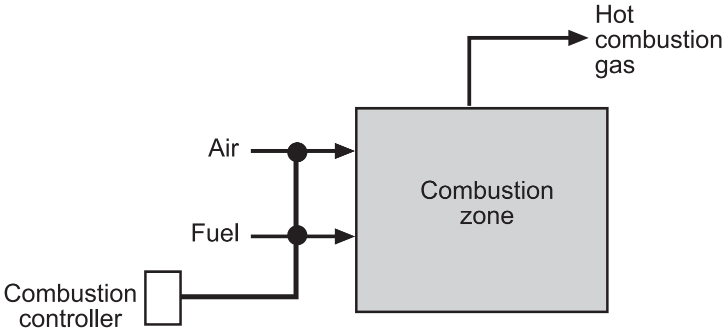


Figure 5-1. A basic boiler

The simplified sketch of a boiler system shown in Figure 5-2 provides a convenient means to define many of the important terms and components applicable to all boilers.

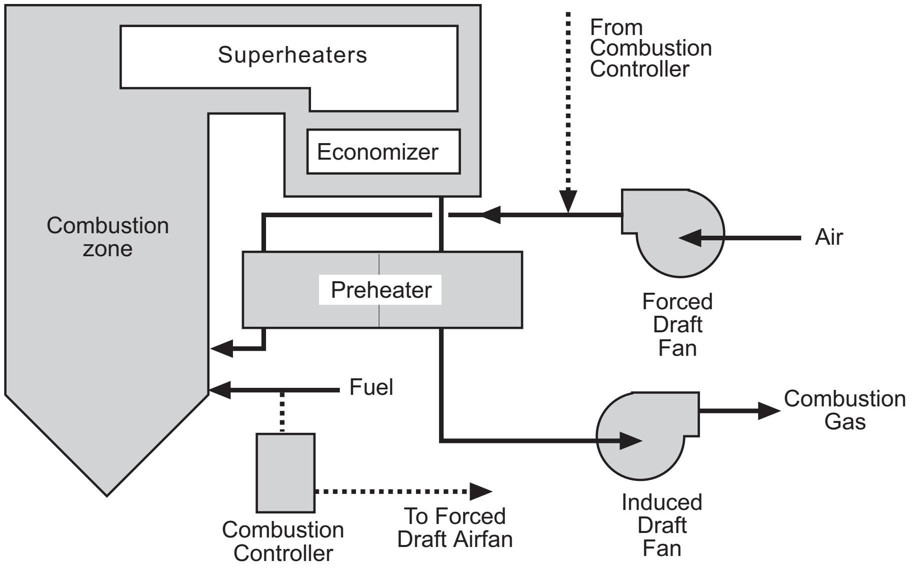


Figure 5-2. Simplified boiler system

The combustion zone or furnace area is where the fuel is ignited and most of the fuel is oxidized. The combustion gases generated by these reactions lose some heat to the boiler walls and tubes as they approach the top of the combustion zone.

Steam is generated in boiler tubes that line the entire combustion zone and are arranged in tube banks throughout the upper portions of the boiler. These tubes are connected to a large drum inside the unit that distribute water and partially heated steam to appropriate areas of the system. Because of the layout and functions, the tube sections and the drum are beyond the scope of this course, due in part to the diversity of boiler designs.

In a series of heat exchangers located beyond the furnace area of the boiler, the hot combustion gases are transferred to steam, condensed feedwater is returned to the boiler, and combustion air enters the boiler. During movement through the heat exchangers, the gas stream temperature drops from a range of 1800°F to 2200°F to a range of 200°F to 400°F.

The majority of the heat remains in the combustion gases until the gases reach the superheater and reheater. There the heat is transferred to steam used to operate the turbines.

Superheater - heats steam to temperatures and pressures well above saturation levels in order to operate the first pass of the steam turbine.

Reheater - heats steam released from the first stage of the turbine to increase the steam pressures and temperatures to the levels necessary for the later stages of the turbine.

After the flue gas cools and passes through the superheater and reheater area, it moves through the economizer. The economizer is a heat exchanger that is used to heat the feed water returning to the boiler.

Economizer - heats feedwater returning from the condensers and returning to the boiler.

After the economizer, the flue gas goes to the air preheater where it heats the combustion air that is going to the pulverizer (for systems that have pulverizers) or other parts of the system.

Air Preheater - heats combustion air for the burner.

The combustion gases then go to an induced draft fan. The induced draft fan is designed to remove all the flue gas generated in the combustion zone or boiler furnace. The gas flow rate generated by this fan is adjusted as needed to maintain a boiler static pressure, termed *boiler draft*, in a range of -0.01 to -0.2 in. W.C. When the draft is in this range, the induced draft fan, often termed *ID fan,* removes combustion gases at essentially the same rate as their formation because of combustion of fuel.

In order to optimize combustion conditions in the boiler, the forced draft (FD) fan controls the combustion airflow to maintain the air-fuel ratios in the range set by the boiler designers and operators.

Combustion air is not supplied in a single stream. In all boilers, the combustion air is divided into two or more separate streams that are introduced into the boiler at different locations to provide optimal combustion conditions. For each of the major types of boilers in this section, combustion air supply and fuel burning equipment are discussed. Fuel burning equipment (burners, grates, and fluidized beds) is discussed later in this section.

Total combustion air flow needed for complete combustion of the fuel is termed the *stoichiometric requirement*. This is the theoretical amount of air needed to fully convert the carbon, hydrogen, and sulfur in the fuel to carbon dioxide, water vapor, and sulfur dioxide. Slightly more than the stoichiometric quantity of air is needed in all boilers, because fuel-air mixing is not perfect. This additional air is called *excess air*. Most boilers operate with relatively low excess air at full boiler load and with moderate rates at mid to low boiler loads. The boiler master often uses oxygen concentration data from the boiler exit to determine if more or less combustion air is needed at a given boiler load to maintain the necessary rate of excess air.

Combustion air is supplied to the boiler by forced draft (FD) fans. The portion of combustion air that is heated in air preheaters (rotary or tube-type) and used in the burners or the fluidized fuel bed is termed the *primary air*. All burner arrangements have a secondary air stream for each burner, and some also have a tertiary combustion air supply for each burner. The secondary and tertiary air stream flow to each of the burners are controlled by air registers.

The excess air rate for boilers is usually in the range of 20% to 100%. The lowest excess air rates are used near maximum boiler load, when combustion conditions are inherently most effective. More excess air is used at low loads to ensure complete combustion, despite reduced gas temperature, mixing, and turbulence.

Many fuels used in boilers contain noncombustible mineral material. A large portion of that ash (*bottom ash*) collects in the bottom of the boiler, from which it is periodically removed. A small portion of the fuel ash is entrained in the combustion gases moving through the heat exchange areas of the boiler. This small mineral material is termed *flyash,* and it is collected in particulate matter control systems located downstream of the boiler (not shown in Figure 5-2).

Small quantities of uncombusted organic material are present in both the bottom ash and the flyash. This organic material is measured by heating a sample of the ash to 1450°F in an oxidizing laboratory furnace and measuring the amount of material that is lost. This parameter is called *loss-on-ignition* or LOI.

5.1.1.1 Flue Gas Temperature

Temperature is critical in determining where certain add-on NO_X control devices can be located. Figure 5-3 shows a typical temperature profile for flue gases generated in a boiler. No temperature is shown in the combustion zone, because the temperature is very specific to the type of boiler being used. However, as the flue gas approaches the superheater and reheater, temperatures in the 1800°F to 2000°F range are typical. As the flue gases pass through the economizer, the temperature drops to the 600°F to 700°F range. As the flue gas exits the air preheater the temperature is in the 300°F to 350°F range. Certain boiler heat exchange equipment designs can produce a flue gas temperature that is lower than this range. However, there are practical limitations to flue gas temperature reduction.

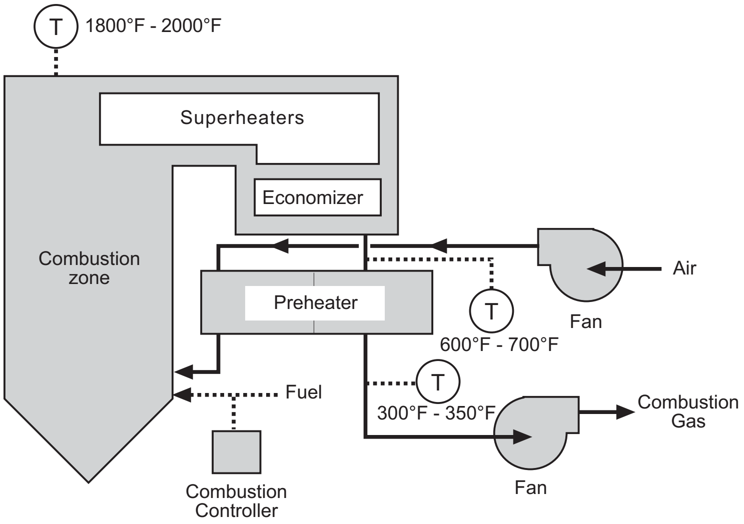


Figure 5-3. Typical gas temperatures in a pulverized coal-fired boiler

5.1.1.2 Dew Point

The first such temperature limitation is acid *dew point*. This is the temperature at which sulfuric acid (H_2SO_4) will condense from the flue gas stream. In most boilers, the H_2SO_4 concentration in the flue gas is in the range of 1 ppm to 20 ppm. The acid dew point for flue gas with an H_2SO_4 concentration of 1 ppm to 20 ppm is approximately 180°F to 275°F, respectively. If the temperature of the flue gas drops below the acid dew point, acid deposition or formation is likely to occur on the colder metal surfaces, causing corrosion of the equipment and significant material damage to the unit. Temperatures are not uniform throughout the boiler and variations of 30°F to 50°F can occur from one side of a duct to the other. Because of this phenomenon, a safety margin is provided by designing boilers for gas temperatures well above the acid dewpoint in order to avoid corrosion problems associated with acid deposition.

The *moisture dew point* can also create a gas temperature reduction limit for some boiler applications. One of the main reaction products for all fuel combustion sources is water vapor. Moisture concentrations from 4% to 9% are common for many boilers. If the flue gas temperature beyond the preheater were to drop to the 120°F to 160°F range, the moisture in the flue gas would condense and could cause corrosion problems.

Air infiltration into a boiler can have a significant impact on the combustion gas temperatures within the boiler. *Air infiltration* refers to the unintended leakage of air into the system. Infiltrating ambient air is much cooler than the flue gas, resulting in gas temperatures considerably below design levels.

Air infiltration conditions could result in gas temperatures below the acid dew point and the moisture dew point.

Air infiltration is a result of boiler normal operation. Boilers are operated at very high temperatures and are routinely cooled during shutdown. The expansion and contraction associated with this heating and cooling can cause cracks and gaps in the boiler casing (walls). Because most boilers are operated under negative pressure, these cracks and gaps allow air to enter the system.

5.1.2 Coal-Fired Boilers

Three major types of coal-fired boilers include pulverized, cyclone, and stoker. They differ with respect to the size of fuel required and the way the fuel is introduced and burned.

Immediately before injection to a pulverized boiler, coal is pulverized to a state in which at least 70% passes through 200 mesh, which is a size similar to the consistency of talcum powder. The entire size range of this pulverized coal is then injected into the burner, where it can be burned entirely in suspension within the burner flame.

Cyclone boilers utilize coal of particle sizes ranging from 0.06 inch to approximately 0.25 inch, which is considerably coarser than that for pulverized coal. Coarse coal is fired in one or two cyclonic combustion chambers located at the bottom of the boiler.

Stoker boilers are relatively large and have steam capacities ranging from 40,000 lb to more than 400,000 lb of steam per hour. The fuel size can range from less than 1/32 -inch to 1/4-inch diameter. There are two to six independent feeders where coal or wood is moved from the fuel burners into mechanical feeders at the front of the boiler.

5.1.2.1 Pulverized Coal-Fired Boilers

Figure 5-4 shows the burner flames in the combustion zone of a pulverized coal-fired boiler. This figure shows three burners; in reality, most large pulverized boilers have 8 to 40 separate burners in any number of configurations.

> These burners are mounted in a large refractory-lined furnace that is sized for a maximum combustion rate (heat release rate), usually rated in terms of millions of BTUs per cubic foot of furnace volume per hour.

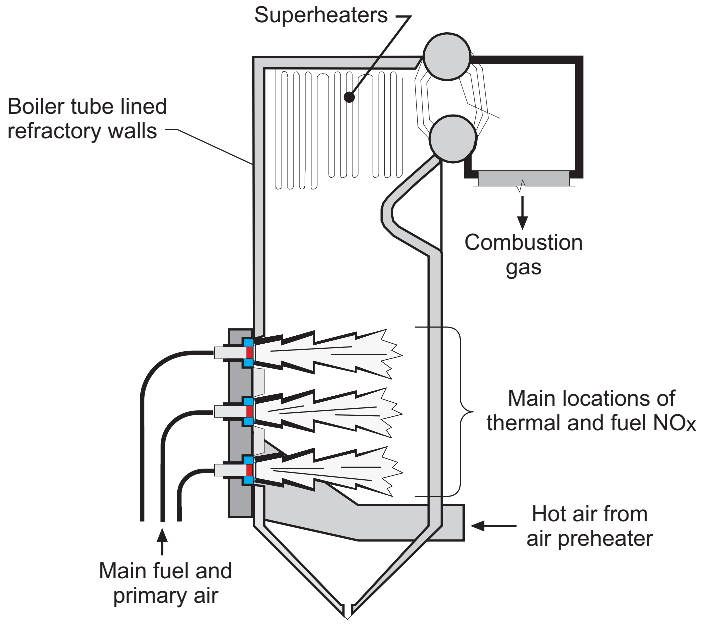


Figure 5-4. Pulverized coal-fired boiler

The figure shows a typical front-fired arrangement, but the burners have various designs that can be divided into three general categories of units (wall-fired, roof-fired, and tangentially-fired), based on the arrangement of the pulverized coal burners.

Pulverized boilers are economical primarily for large industrial and utility power stations.

Wall-Fired (Front) Boilers
All of the burners are mounted on a single wall of the furnace. The width of the furnace is designed to ensure that the burner flames do not impinge on the boiler tube-lined wall on the opposite side of the furnace. Hot gases from the horizontally mounted burners move upwards in the furnace and enter the main heat exchange area of the boiler.

Wall-Fired (Opposed) Boilers
Sets of burners are on two opposite walls. In this case, the furnace width is moderately large to accommodate the horizontally mounted burners and flames extending from each side.

Tangentially-Fired Boilers
Four sets of horizontally mounted burners are in each corner of the boiler. The burner flames extend into the furnace area in a slightly off-center manner to create a spinning movement in the flames from each corner.

Tangentially-fired boilers have slightly low NO_X because of the reduced flame temperatures within the boiler.

The firing configuration has an influence on NO_X emissions and the method by which the emissions are controlled. As shown in Figure 5-4, pulverized coal and primary air travel through burner pipes to the burners. The pulverized coal is suspended in this primary air, which is heated in the preheater. A *coal feeder* delivers coal to the *pulverizer*, which uses attrition type processes to reduce the coal to the required size (i.e., 70% through 200 mesh). The coal feeder and pulverizer are critical steps in the process of combusting coal because delivery of a consistent size of coal to the burners is required for good combustion. This primary air-fuel mixture is mixed with secondary air prior to combustion. Hot flue gases exit the burners and rise vertically as the heat is transferred to the boiler tubes that line the boiler walls. The gases continue through the superheater and reheater.

Typical combustion product gas stream (i.e., flue gas) temperatures were indicated earlier in Figure 5-3. The peak combustion gas stream temperatures in the burner flames can exceed 2,500°F (1370°C). Gases entering the superheater and reheater areas are usually in the range of 1,800°F to 2,000°F (980°C to 1080°C). Flue gas temperatures leaving the air preheater are usually in the range of 250°F to 350°F (120°C to 180°C).

A significant fraction of the ash in the coal is removed as bottom ash. When the ash fusion temperature is relatively high, this ash is entirely in solid form. Units that remove ash in this form are called *dry bottom*. Pulverized coal-fired boilers designed for low ash fusion coals that remove the bottom ash in the molten state are termed *wet bottom*.

Pre-NSPS NO_X emissions varied from 0.5 to 0.8 lb/MMBtu for wall-fired coal boilers and 0.4 to 0.7 lb/MMBtu for tangentially-fired coal boilers. Since 1970, considerable progress has been achieved in the reduction of NO_X emissions from these sources. Various combustion modification techniques have been demonstrated to be effective and include the following:

- Low excess air combustion
- Off-stoichiometric combustion
- Flue gas recirculation
- Low NO_X burners
- Gas reburning

The operating principles and general NO_X reduction efficiencies for these combustion modifications are discussed in Chapter 6, *Combustion Modifications*; Chapter 7, *Low NO_X Burners*; and Chapter 8, *NO_X Reburning*.

5.1.2.2 Cyclone Boilers

Cyclone boilers are similar to pulverized boilers, in that the hot flue gases rise vertically and lose heat to the boiler tubes and other heat exchange equipment. However, cyclone boilers have fewer burners at the base of the unit and the coal is larger than coal that is charged to a pulverized boiler. Because of these differences in operation, the cyclone boiler requires a completely different burner that results in higher operating temperatures.

> The combustion chamber is refractory lined because of the intense heat release rates achieved in these units. Heat exchange equipment used in cyclone boilers is very similar to that used in pulverized coal-fired boilers. However, there are no boiler tubes in the combustion chamber because of the extreme temperatures and abrasive conditions created by spinning ash in the cyclonic burner flames.

A cyclone boiler is illustrated in Figure 5-5.

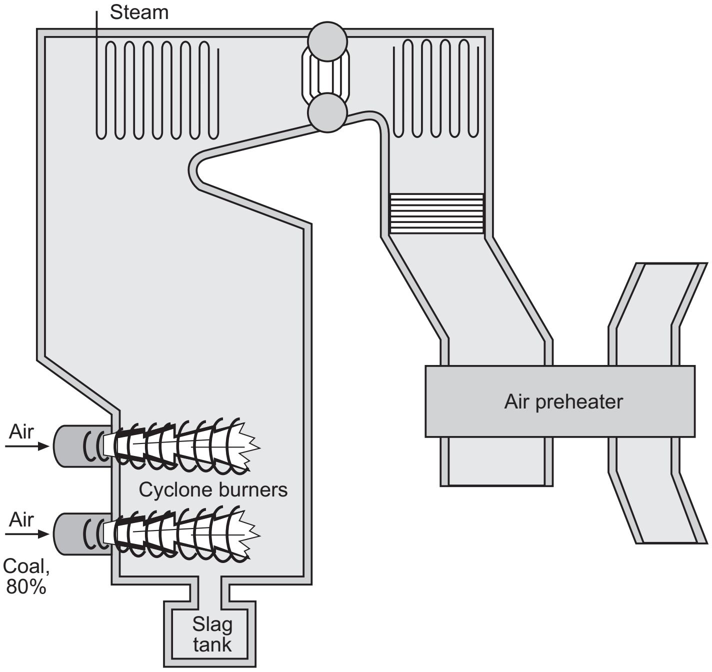


Figure 5-5. Cyclone boiler

The flue gas temperature in the cyclone boiler exceeds the fly ash fusion temperature (2100°F to 2600°F). As a result of these high temperatures, some of the ash in the flue gas becomes molten and drains into the slag tank at the bottom of the boiler, where it is quenched and removed. Because of this high temperature operation, the cyclone boiler is called a *wet bottom* boiler.

Because of the high gas temperatures achieved in the cyclonic chamber, relatively high NO_X emissions of 1.1 lb/MMBtu to 1.7 lb/MMBtu are generated. Most cyclonic boilers presently in operation were installed prior to the 1971 promulgation date for Subpart D (applicable to fossil fuel-fired boilers) and therefore do not have to comply with the regulation. Because of the limited available NO_X suppression technology available at that time, cyclonic boilers were not able to comply with this standard.

5.1.2.3 Spreader Stoker Boilers

Spreader stoker boilers can charge coal, wood or refuse-derived fuel (RDF).

They can change load rapidly and are often used in process operations where cyclic operations impose rapidly changing steam demands.

An example of a spreader stoker boiler is provided in Figure 5-6. The fuel is charged with a spreader stoker feeder. Most spreader stoker boilers have two to six spreader stoker feeders. The feeder flings the fuel outward and distributes it uniformly on a grate that moves toward the front of the boiler. Combustion air is introduced through a single undergrate air plenum and a set of overfire air

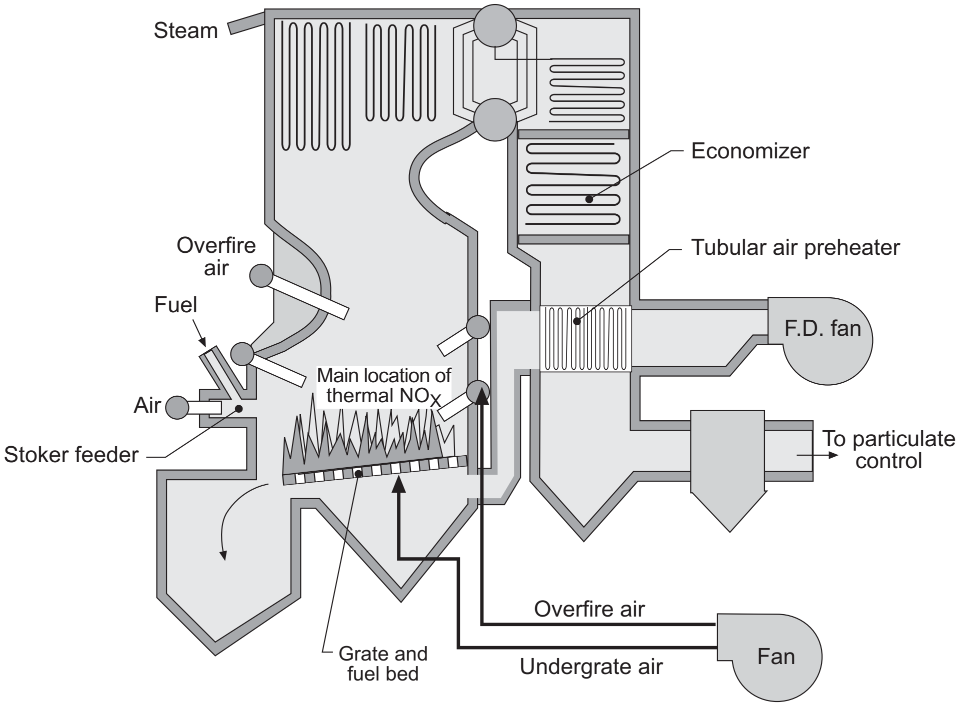


Figure 5-6. Coal-, wood-, or RDF-fired spreader stoker boiler

nozzles on the front and back walls of the boiler. Overfire air ports are usually located at several elevations on the back wall and on at least one elevation on the front wall. These ports provide air for combustion of the fuel being burned in suspension and for combustion of volatile matter released from the coal or wood burning on the grates. The combustion controller or boiler master controls the total air entering the boiler from both the air ports and the undergrate and can change the ratio of overfire air to undergrate air.

Excess air rates range from 40% to 50% at maximum boiler load to up to 100% at low boiler load.

Approximately 30% of the fuel or waste is burned while the particles are in suspension during feeding. The remainder of the fuel burns on the bed.

Flue gases rise vertically through a series of heat exchange equipment. Most spreader stoker boilers are equipped with a baghouse or electrostatic precipitator for controlling particulate matter emissions.

Uncontrolled NO_X emissions from spreader stoker boilers and other stoker boilers range from 0.3 lb/MMBtu to 0.5 lb/MMBtu. These emissions depend in part on the fuel nitrogen levels and the characteristics of combustion.

5.1.1.4 Fluidized Bed Boilers

A wide variety of fluidized bed boilers have been placed in commercial service since the early 1980s. These boilers combust fuels in a fluidized bed of limestone and fuel particles; there are no fuel burners or grates. The bed is fluidized by the upwards-moving combustion air and by the combustion gases generated in the bed. NO_X formation is minimized (0.2 to 0.4 lb/MMBtu) because combustion occurs at temperatures of 1600°F to 1800°F, well below the peak flame temperatures present in burner flames of pulverized coal-fired boilers and above the grates of some spreader stoker boilers. Sulfur oxide emissions are minimized because of the reaction of sulfur dioxide with the limestone in the bed.

There are two main types of fluidized beds in commercial service: bubbling beds and circulating fluidized beds (CFB). In bubbling beds, one or more beds of material approximately three feet in depth (static conditions) are used for fuel combustion. All of the bed materials, with the exception of flyash entrained in the combustion gases, remain in the boiler furnace area. In CFBs, a portion of the bed is entrained in the combustion gas stream and is initially treated in a set of large-diameter cyclones. Large limestone and fuel particles are returned to the bed. Both types of fluidized bed boilers generally use high efficiency particulate matter control systems, such as electrostatic precipitators or fabric filters, for control of the flyash emissions.

One of the main advantages of fluidized bed boilers is their ability to handle a wide variety of fuels with no significant combustion problems and minimal fuel pretreatment requirements. For these reasons, fluidized boilers are often used in applications where the materials being burned are too variable or have conditions that preclude their use in conventional boilers.

5.1.3 Oil- and Gas-Fired Boilers

A large industrial or utility scale oil- or gas-fired boiler is very similar to a pulverized coal boiler. An array of burners is mounted in a boiler tube-lined furnace area. Heat exchange and heat recovery equipment is used to generate steam and to reduce the flue gas temperatures. NO_X emissions from gas- and oil-fired boilers are moderately low due, in part, to the low fuel nitrogen levels. Post-NSPS uncontrolled NO_X emissions are usually in the range of 0.2 4 lb/MMBtu to 0.4 lb/MMBtu.

The primary differences between oil- and gas-fired boilers and pulverized coal boilers are the geometry of the furnace area, the volume of the furnace, and the type of burners. Essentially all of the small quantities of ash (oil-fired only) entering with the fuel are emitted as flyash. The flyash from oil-fired units usually has a different composition from that generated in coal-fired boilers. In addition, gas-fired units have negligible ash emissions.

Three main types of oil are used in large installations: No. 2, No. 5 and No. 6 oil. No. 2 oil (a distillate oil) has low sulfur and ash content and has a lower heating value than less refined fuels, such as No. 5 and No. 6 oils. However, No. 2 oil is also more expensive. No. 5 oil and No. 6 oil are residual oils with relatively high sulfur and ash contents. Both require facilities equipped with preheating equipment and, in the case of No. 6 oil, the ability to handle high-viscosity fuel.

Gas- and oil-fired boilers usually operate at rates of excess air ranging from 5% to 10% at maximum boiler load to 10% to 25% at low boiler load. Higher excess air rates are needed at low boiler load because of the reduced furnace temperatures, reduced gas mixing, and reduced turbulence.

Combustion modifications appropriate for oil-fired boilers are similar to those used for pulverized coal-fired boilers: low excess air operation, off-stoichiometric firing, flue gas recirculation, low NO_X burners, and gas reburning.

5.2 STATIONARY INTERNAL COMBUSTION ENGINES

Internal combustion (IC) engines operate in either rotary or reciprocating motion. Gas turbines are rotary engines. Reciprocating engines produce mechanical work from a rotating shaft that is powered by moving pistons. Stationary reciprocating IC engines include generators, pumps, industrial sweepers and scrubbers, and material handling equipment, such as conveyors.

5.2.1 Gas Turbines

5.2.1.1 Overview

All gas turbines consist of a compressor, combustor, and power turbine. Air is compressed up to 30 atmospheres in the compressor and mixed with fuels such as natural gas and distillate oil. Following combustion, the hot expanded gas is sent to the power turbine. The turbine rotates to generate electricity and steam that is used for a variety of applications such as peaking service, cogeneration systems, gas compressor station operation, and emergency power generation. The options available for minimizing pollutant emissions vary depending, in part, on the operating conditions necessary for these different applications.

Peaking Service Units
These units are used primarily for satisfying peak electrical demand and often operate for a relatively small number of hours per year. Exhaust gases from these units are often discharged directly to the atmosphere and are difficult to control because of limited operating time and high temperatures in the flue gas stream.

Cogeneration System Units
Relatively large and operating on a relatively stable load, cogeneration system units are adaptable to advanced pollutant control techniques. To a certain extent, the increased number of cogeneration units is due to the Public Utilities Regulatory Policies Act, which mandated that utilities must purchase excess electrical power generated at these stations.

Gas Compressor Stations
These are relatively small units used to provide electrical power for the compressor at remote pipeline stations.

Emergency Service Gas Turbines
These gas turbines can be used to provide electrical power for emergency pumps and are usually not subject to air pollution control requirements. There are several different designs for these gas turbines.

5.2.1.2 Simple Cycle Turbines

Figure 5-7 is a schematic of a simple cycle gas turbine. The fuel is burned in a parallel set of combustion chambers. Exhaust gases at temperatures of 900°F to 1,000°F (480°C to 540°C) are expelled directly into the atmosphere. This type of arrangement is used in some old installations intended for peaking service. Simple cycle turbines have relatively low thermal efficiency because of the loss of sensible heat in the hot exhaust gases. These turbines may also include a heat recovery steam generator to produce low-pressure steam.

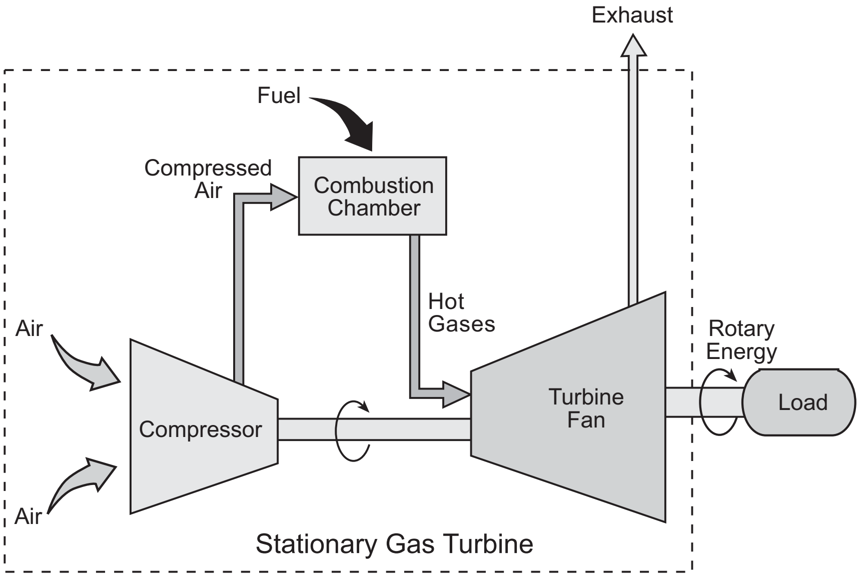


Figure 5-7. Simple cycle gas turbine

5.2.1.3 Combined Cycle Gas Turbines

A simplified schematic of a combined cycle gas turbine system is shown in Figure 5-8. The waste heat boiler section is a conventional boiler tube heat exchanger. This boiler generates steam that can be used to generate electrical power and can also be exported for process use or space heating. When both electrical power and steam are generated, the system is termed a *cogeneration unit*.

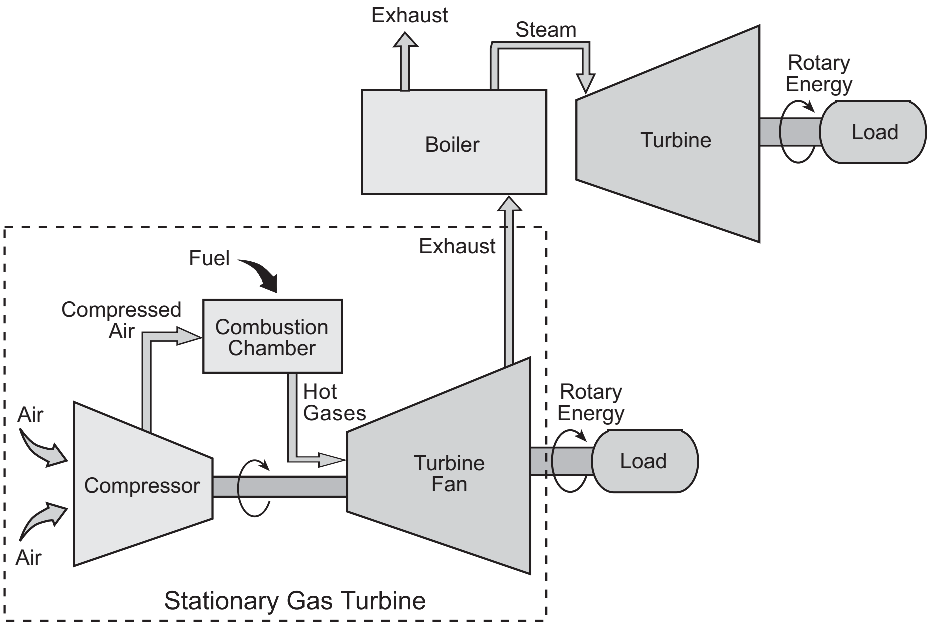


Figure 5-8. Combined cycle gas turbine

Combined cycle turbines can be equipped with a duct burner to increase the gas temperature of exhaust gases entering the waste heat boiler. Duct burners generally use natural gas as a fuel. They increase the gas temperature to more than 1800°F (980°C) so that more steam can be generated. Oxygen in the turbine exhaust gas stream is used for combustion of natural gas in the duct burner.

A conventional combustor for a gas turbine is shown in Figure 5-9. A number of these combustors are used on the gas turbine to generate the high temperature and high-pressure exhaust gases necessary for the turbine located downstream. Combustion air is supplied under pressure from the upstream compressor.

Conventional combustors use a diffusion-type flame. The air and fuel are mixed in proportions that are very close to the stoichiometric level. Accordingly, the peak gas temperatures are very high. Typical NO_X concentrations at full load average 175 ppm, with some units exceeding 400 ppm.

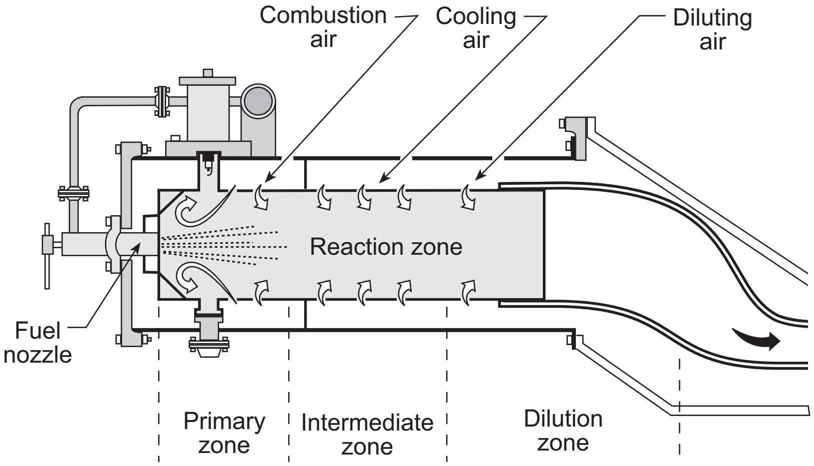


Figure 5-9. Conventional gas turbine combustor

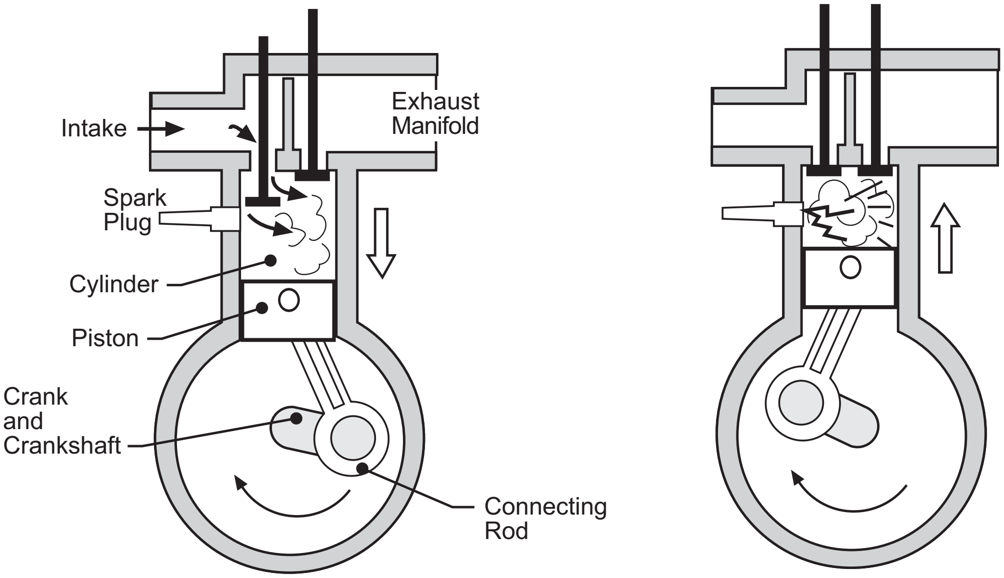
5.2.2 Reciprocating Engines

5.2.2.1 Overview

Reciprocating engines are used in various industrial applications. An air or fuel-air mixture is compressed in a cylinder above the piston and ignited by one of two methods: compression ignition (CI) and or spark ignition (SI). Upon combustion, the piston is forced through the cylinder. A crankshaft turns the shaft of the piston. The piston then returns to the original position, exhausting the combustion products, and the cycle is repeated. Reciprocating internal combustion engines can accomplish this cycle in either two or four strokes. Reciprocating engines often have NO_X emissons ranging from 2.3 lb/MMBtu to 3.2 lb/MMBtu.

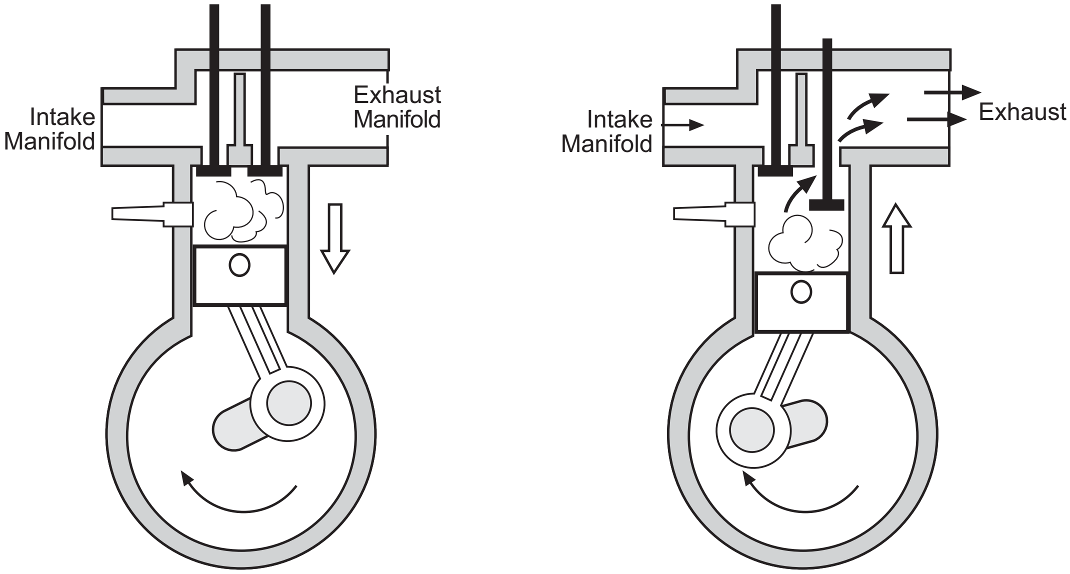
5.2.2.2 Four-Stroke Engines

During the intake stroke, the air or air-fuel mixture is drawn into the cylinder by the downward movement of the piston. The air or air-fuel mixture is compressed to raise the air temperature for the compression stroke. The gas in the cylinder is then ignited, thereby forcing the piston down and transferring the energy to the crankshaft. The final stroke expels the exhaust gases from the cylinder. The basic operation of an SI four-stroke stationary internal combustion engine is illustrated in Figure 5-10.



1. INTAKE STROKE
Intake valve opens, admitting charge of fuel and air. Exhaust valve closed for most of stroke.

2. COMPRESSION STROKE
Both valves closed. Fuel-air mixture is compressed by rising piston. Spark ignites mixture near end of stroke.



3. POWER OR WORK STROKE
Fuel-air mixture burns. Increasing temperature and pressure and expansion of combustion gases drives piston down. Both valves closed. Exhaust valve opens near end of stroke.

4. EXHAUST STROKE
Exhaust valve opens. Exhaust products are displaced from cylinder. Intake valve opens near end of stroke.

Figure 5-10. A four-stroke, spark-initiated engine cycle

5.2.2.3 Two-Stroke Engines

The two-stroke internal combustion engine completes the same basic cycle as a four-stroke engine, but in only two strokes. The piston compresses the air or air/fuel mixture as it moves upward in the cylinder. The power stroke occurs after the gas is combusted. Then the piston moves upward again, replacing the combustion products with air or an air-fuel mixture.

5.2.2.4 Compression Ignition Engines

All diesel engines operate with compressed ignition. Air is compressed and heated above the autoignition temperature of diesel fuel oil. The fuel is then added, causing spontaneous combustion. Natural gas can also be used for CI engines. However, because the auto ignition temperature of natural gas is higher than temperatures present in the cylinder, a small amount of diesel fuel must be added to initiate combustion.

Because fuel is absent during compression, CI engines have higher compression ratios than SI engines. Pressure ratio increases with the compression ratio. Thermal efficiency is directly related to the pressure ratio, making CI engines more efficient than SI engines.

5.2.2.5 Spark Ignition Engines

SI engines initiate combustion by an electrical spark. Prior to injection, fuel and air are mixed by a carburetor for gasoline, or at the intake valve for natural gas. The fuel-air mixture is added to the cylinder and ignited near the end of the compression stroke. SI engines can withstand load changes and higher pressures than CI engines. This is why gasoline-fueled automobiles are able to accelerate quickly.

5.3 MUNICIPAL WASTE INCINERATORS

Waste nitrogen levels can be high and can vary substantially on a seasonal basis. Yard waste and other vegetation are the primary nitrogen-containing materials entering the municipal incinerator feed stream.

The sloped, reciprocating grate incinerator shown in Figure 5-11 is a common type of municipal waste incinerator. Wastes move through the unit because of the slope of the grate and the reciprocating (back-and-forth) movement of the grate sections. Wastes are deposited on the upper sections of the grate from a chute that is loaded by an overhead crane.

At least four undergrate plenums are used to adjust the underfire air rates to the different rates of combustion in the incinerator. Low airflow rates are used in the first zone (drying and ignition) and in the last zone (ash burnout). As indicated in Figure 5-11, the airflow rates are adjusted using dampers in the air supply ducts to the plenums. Ash and residue are discharged from the grate into an ash pit, where ash is quenched and continually removed by a conveyor.

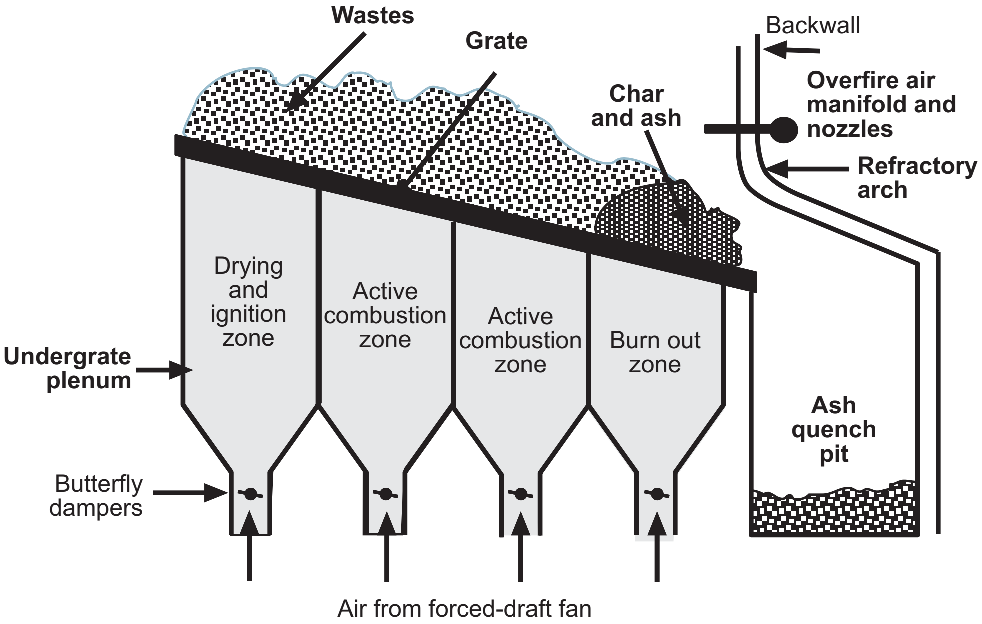


Figure 5-11. Municipal waste incinerator

Other municipal waste incinerator systems in commercial operation include rotary kilns, modular (two chamber) starved air incinerators and modular stoichiometric incinerators.

Review Exercises

1. What is the typical temperature of gases leaving the economizer of pulverized coal-fired boilers?
   a. 250°F to 400°F
   b. 400°F to 600°F
   c. 600°F to 700°F
   d. 800°F to 1200°F
   e. 1200°F to 1800°F
   f. 1800°F to 2400°F

2. What is the typical temperature of gases leaving the air preheater of a pulverized coal-fired boiler or a gas-fired boiler?
   a. 300°F to 350°F
   b. 350°F to 600°F
   c. 600°F to 800°F
   d. 800°F to 1200°F
   e. 1200°F to 1800°F
   f. 1800°F to 2400°F

3. Is the excess air rate higher or lower when boiler load is at its maximum?
   a. Higher
   b. Lower
   c. Excess air rate is not related to the boiler load.

4. What is the normal range of excess air levels in a spreader-stoker boiler at maximum load?
   a. 2% to 25%
   b. 25% to 40%
   c. 40% to 50%
   d. 50% to 75%
   e. 100% to 125%

5. What is the normal range of excess air levels in a gas-fired boiler?
   a. 0% to 1%
   b. 1% to 5%
   c. 5% to 25%
   d. 20% to 50%
   e. 50% to 100%
   f. 100% to 200%

6. What type of coal-fired boiler has the highest NO_X generation rates?
   a. Pulverized coal-fired boiler
   b. Spreader stoker boiler
   c. Fluidized bed
   d. Cyclone-fired boiler
   e. None of the above

7. Which of the following describes a large coal-fired boiler that has burners located at the corners of the combustion chamber?
   a. Opposed-fired boiler
   b. Tangentially-fired boiler
   c. Ceiling-fired boiler
   d. Stoker boiler
   e. Circulating fluidized bed boiler
   f. None of the above

8. For which of the following gas turbine application(s) is NO_X control generally not applied?
   a. Cogeneration
   b. Peaking service
   c. Emergency service
   d. Gas compressor stations
   e. None of the above

9. A facility that generates both electrical power and steam is a ________.
   a. Cogeneration unit
   b. MCI
   c. Spreader stoker boiler
   d. Combined cycle gas turbine
   e. None of the above

10. In which type of stationary internal combustion engine is *only* air compressed in a cylinder above the piston during the compression stroke?
    (Select all that apply.)
    a. Two-stroke reciprocating SI engine
    b. Four-stroke reciprocating CI engine
    c. Rotary engine
    d. None of the above
    e. All of the above

6 Combustion Modifications

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Identify the two main combustion parameters underlying combustion modifications to control NO_X.

2. Identify four combustion modifications used to control NO_X formation and compare their advantages and disadvantages.

3. Describe the relationships of excess air and combustion efficiency to NO_X control.

4. Name the factors that limit the effectiveness of combustion modifications to suppress NO_X formation.

6 Combustion Modifications

Modifications to the combustion system lower NO_X emissions by suppressing NO_X formation. Therefore, combustion modifications are a logical first step in the reduction of NO_X emissions. They were the primary NO_X control technique applied to a wide array of combustion systems from the early 1960s through to the early 1990s.

One or more types of combustion modification are now being used in combination with a variety of add-on control systems and low NO_X burners to achieve more stringent NO_X emission limitations.

6.1 PRINCIPLES OF COMBUSTION MODIFICATIONS

The principles of combustion modifications are based on NO_X formation chemistry and focus on minimizing peak temperatures and the residence time at the peak temperatures. Combustion modification techniques also attempt to minimize the availability of oxygen at peak temperatures, while minimizing oxygen in the fuel devolatilization zone.

Temperature is a primary factor in NO_X control. NO_X is controlled by kinetics, not equilibrium, which means that the critical parameter in the formation of NO_X is the *rate* of formation, rather than the *total* formation that could be achieved if all reactions occur. Formation kinetics follow the Arrhenius form, which is proportional to $e^{-1/T}$. As a result, the rate at which the reaction occurs is strongly dependent on temperature. The goal is to reduce NO_X formation by minimizing the gas temperature and its residence time at that temperature.

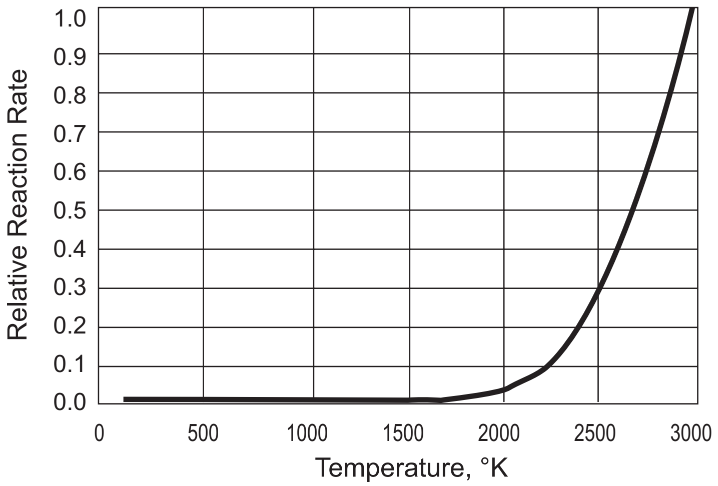


Figure 6-1. Relative NO_X formation rates based on the Arrhenius relationship

Figure 6-1 shows the form of the Arrhenius rate as a function of temperature. The reaction begins between 1500 °K to 2000°K and accelerates after the temperature has reached 2000°K. Therefore, maintaining a temperature below 2000°K can significantly reduce the reaction rate, resulting in the formation of less NO_X.

NO_X formation can also be reduced by minimizing the amount of available oxygen. NO_X is formed when nitrogen, either in the combustion air or the fuel, reacts with oxygen in the atmosphere (some oxygen could also originate in the fuel).

In either approach, the main strategy is to minimize the interactions of N_2 and O_2 — especially at high temperatures — without upsetting the interactions of the fuel and the oxygen. High temperature is necessary for flame stability and good heat transfer, while low temperature is favorable for minimizing NO_X formation. Less O_2 and minimal mixing of O_2 and fuel also result in less NO_X formation, but all these factors must be balanced in order to maintain efficient combustion. Otherwise, performance issues may arise. Flame instability, increased carbon monoxide (CO), increased carbon-in-ash, and lower thermal efficiency are a few of the indications that performance is being undermined.

As shown in Figure 6-2, for a typical coal-fired boiler, increased O_2 levels result in an increase in NO and dramatic decrease in CO. The optimal operating point on this graph is the “CO knee” where the CO begins a rapid increase. It should be noted that the relationship between oxygen level and unburned carbon level follows a similar relationship as CO.

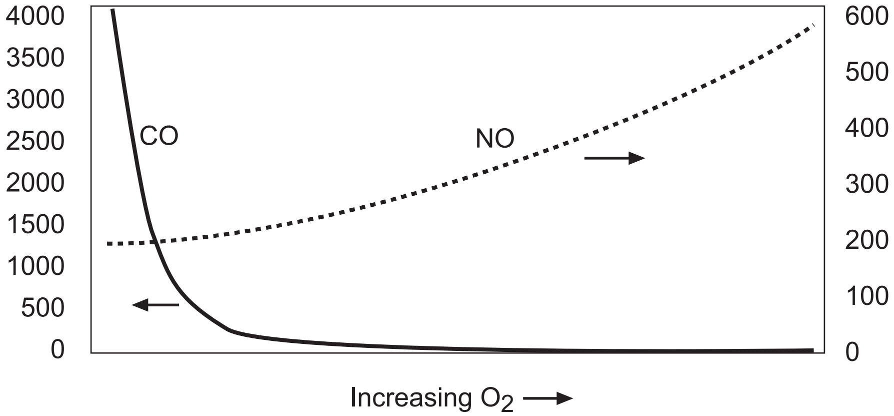


Figure 6-2. Relationship between CO formation, NO_X formation, and oxygen concentrations at low oxygen concentrations

Stoichiometry is the measure of the amount of air (or oxygen) used to combust each pound or mole of fuel. A stoichiometric ratio of one means that the minimum amount of air is being used to achieve complete burnout or combustion of the fuel. In this case, the entire amount of carbon in the fuel is being converted to CO_2 instead of CO.

Burning with as little air as possible serves a number of purposes. First, it reduces the fan power required to move the air through the unit. It also reduces the amount of nitrogen introduced into the unit, which reduces the amount of NO_X that is formed.

Incremental mixing of the fuel and air (i.e., *staging*) allows the unit to operate fuel-rich and then fuel-lean. During fuel-rich operation the temperature is reduced and the interaction between O_2 and N_2 is minimized. Operating in a fuel-lean (air-rich) mode allows all of the fuel to be completely burned. There are practical limits on operating in this manner because of the limited residence time and the ability to maintain a stable flame.

At a stoichiometric ratio of 1, more N_2 is available for combustion than any other compound. This is because N_2 comprises approximately 80% of atmospheric air, so for each molecule of O_2 in combustion air there are four molecules of N_2. The objective is to balance the amount of O_2 and fuel so that the fuel is burned completely without introducing too much air (O_2, N_2, and other constituents). A stoichiometric ratio of less than 1 allows more fuel for reaction with the O_2. There is also a reduced temperature that leads to less NO_X formation. However, the final stoichiometric ratio must be greater than 1 for the CO and hydrocarbons to be completely burned, and more air must be added to accomplish this.

6.2 COMBUSTION MODIFICATION TECHNIQUES

Initial efforts to control nitrogen oxides in utility and industrial boilers concerned combustion modifications. Boiler modifications involve changes to the fuel firing equipment and operating conditions to suppress the formation of nitrogen oxides. There are four major categories of combustion modification techniques.

- Low excess air (LEA) combustion
- Off-stoichiometric combustion [Burners Out Of Service (BOOS), Biased Firing, and Overfire Air (OFA)]
- Flue Gas Recirculation
- Reduced Air Preheat

The fundamental objective of all four techniques is to suppress NO_X formation by minimizing (1) the residence peak temperatures, (2) the peak oxygen concentration, and (3) the residence time of the combustion products in peak temperature-peak oxygen concentration areas. These modifications have a direct impact on thermal NO_X and fuel NO_X formation rates.

NOTE: The broadcast video presentation includes the use of low excess air in the off-stoichiometric combustion category. However, this manual addresses LEA as a separate category, because LEA is generally the first combustion modification that is implemented to attain NO_X reductions. In practice, LEA is often used in combination with some or all of the off-stoichiometric techniques. For this reason, the video presentation elected to include it in the off-stoichiometric category.

6.2.1 Low Excess Air Combustion

Using low excess air (LEA) is the easiest approach to implement for reducing NO_X emissions from combustion sources. LEA firing practices reduce NO_X emissions by reducing the amount of surplus oxygen in the portion of the burner flame where gas temperatures are at a maximum. This reduces the peak temperature of the flame and the available O_2, which inhibits the reactions responsible for both thermal and fuel NO_X.

Use of LEA also reduces the total amount of air introduced into the boiler. This results in an increased thermal efficiency of the boiler system, provided that the stoichiometric ratio is maintained at the level required for complete combustion. The use of LEA can also result in higher CO emissions or unburned carbon resulting in a decrease in efficiency. However, LEA yields minimal NO_X reductions.

LEA is easy to implement because adjustments to the combustion controls are the only physical modifications required. Consequently, LEA is one of the most uniformly applicable combustion modification techniques.

LEA can be applied to both suspension and stoker-fired boilers and it provides modest NO_X reductions for coal, residual oil, distillate oil, and natural gas fuels.

The excess air rates are adjusted by making changes in the combustion control system (boiler master). In some cases, upgrades to the oxygen monitoring system and combustion control instrumentation are helpful in maintaining optimum boiler operation after decreasing the excess air rates.

Combustion air provided by the forced draft fans is controlled by the boiler master is not necessarily the only air available to participate in NO_X formation reactions. Air can also leak into the combustion chamber. The leakage problem is caused, in part, by thermal expansion and contraction during start-up and shutdown. The static pressures in the areas of the boiler prone to leakage are usually –0.05 to –0.20 in. W.C.

If the flue gas O_2 and CO concentrations are known, then the percent excess air can be calculated using the following equation.

$$\%EA = \left[\frac{\%O_2 - 0.5\,\%CO}{0.264\,\%N_2 - (\%O_2 - 0.5\,\%CO)}\right] * 100 \qquad \text{Equation 6-1}$$

Where:

0.264 = Ratio of O_2 to N_2 in air v/v.

Equation 6-1 is applicable to sources that burn fuels with no appreciable amounts of N_2, such as coal, oil, and natural gas. Excess air levels for coke oven and blast furnace gases can not be calculated using this relationship. This equation assumes that ambient air is the source of O_2.[1]

The amount of air needed to complete combustion can also be accurately calculated based on the amount of fuel being fired and the ultimate analysis of the fuel. The ultimate analysis provides the total quantity of carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine, ash, and moisture in the fuel. The amount of oxygen needed for combustion can then be calculated based on the following stoichiometric relationships.

$$C + O_2 \rightarrow CO_2 \qquad \text{Reaction 6-1}$$

$$2H + \frac{1}{2}O_2 \rightarrow H_2O \qquad \text{Reaction 6-2}$$

$$S + O_2 \rightarrow SO_2 \qquad \text{Reaction 6-3}$$

In calculating the total oxygen required, the amount of oxygen already present in the fuel is subtracted, because this oxygen will contribute to the conversion of the fuel to its final reaction products: CO_2, H_2O, SO_2, and NO_2.

Excess air is expressed as a percentage of the theoretical air calculated for complete combustion. For example, a 40% excess air level means that the amount of air provided is 140% of the total theoretical air requirement.

There are definite limitations to LEA operation. Very low excess air firing can produce increased particulate and CO emissions, and fouling and slagging of boiler tube surfaces can occur. This is indicated by the general performance curve shown as Figure 6-6.

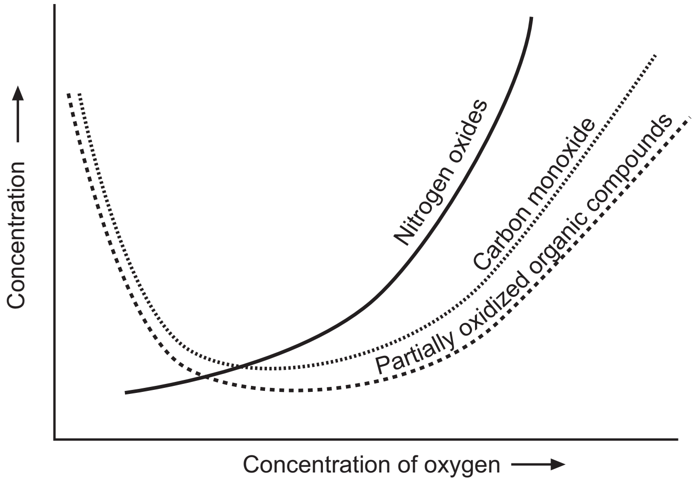


Figure 6-3. Relationship between CO emissions, NO_X formation, and oxygen concentrations at low and high oxygen levels

NO_X emissions generally decrease with decreasing excess air. As the oxygen levels decrease, there is a level at which combustion is not complete and pollutants such as smoke, carbon monoxide, and volatile organic compounds increase, as indicated in the general relationship previously shown as Figure 6-2. The minimum level is unique to each type of boiler application. The optimum point for LEA is reached when an increment of excess air reduction (e.g., 0.1% oxygen) is equal to the loss from the increase in ppm of CO.

Figure 6-3 also illustrates that smoke, CO, and volatile organic compounds increase if the oxygen level is too high. These emissions are caused by cooling of the combustion chamber caused by the use of excessive combustion air and/or air infiltration into the combustion chamber.

Average NO_X reductions of 16% to 20% can be achieved on gas- and oil-fired utility boilers when the excess air is reduced to a level between 2% and 7%.[2] NO_X reductions averaging around 20% can be achieved on coal-fired utility boilers if the excess air is reduced to the 20% level.[3]

6.2.2 Off-Stoichiometric Combustion

During off-stoichiometric combustion or staged combustion, combustion occurs in two zones. In one zone, the fuel is fired with less than the stoichiometric amount of air (stoichiometric ratio or $SR < 1$). This creates a fuel-rich condition in the region of the primary flame. The second zone is an air-rich area where the remainder of the combustion air is introduced to complete the combustion of the fuel ($SR > 1$). The temperature in the primary flame zone is not as high as with conventional firing because combustion is incomplete.

Off-stoichiometric combustion is an effective technique for controlling both thermal and fuel NO_X because of its ability to control the mixing of fuel with combustion air. The NO_X reduction effectiveness is limited by the same factors that limit low excess air operation, namely, for the formation of carbon monoxide and partially oxidized organic compounds, soot-related boiler tube fouling, and boiler tube fire side corrosion. The latter problem can occur when the unit is firing sulfur-containing coal or residual oil.

Overfire Air

Staged combustion can be accomplished by using overfire air (OFA) ports. These are separate air injection nozzles located above the burners as indicated in Figure 6-4. The burners are operated fuel-rich, and the overfire air ports maintain the remainder of the combustion. Approximately 15% to 20% of the combustion air flow is diverted to the over-fire air ports.[4]

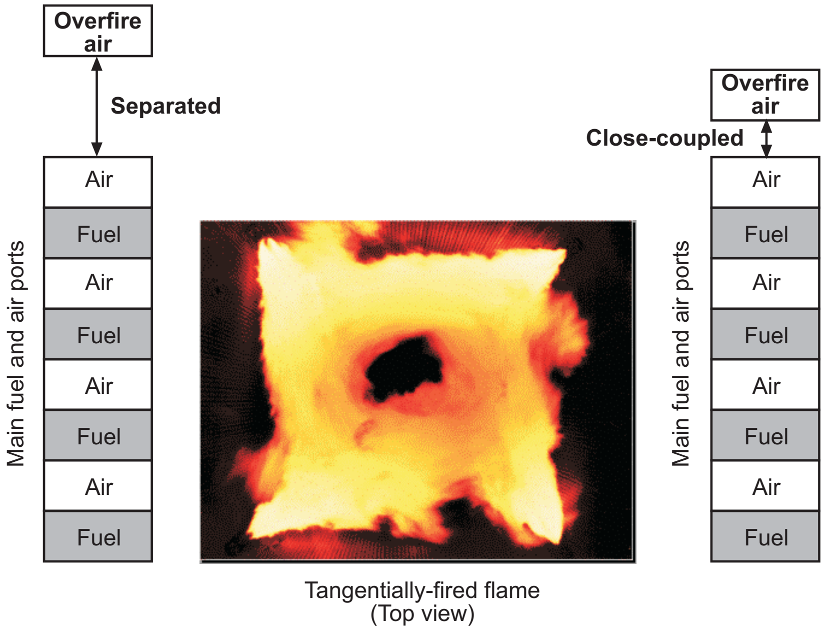


Figure 6-4. OFA in tangentially-fired units

Overfire air combustion modifications require the penetration of the boiler wall by new air ducts and usually requires changes to the air handling system in order to deliver the air to the secondary combustion zone.

> Furthermore, there must be sufficient space above the burners and before the heat exchange area of the boiler to provide sufficient time for the combustion reactions. Because of this limitation, this approach is not possible on some existing coal-, oil-, and gas-fired suspension-type boilers.

As with LEA, OFA may increase CO or unburned hydrocarbon emissions. It is also applicable to process heaters by using air lances rather than changing the boiler configuration. OFA for small boilers and process heaters can be accomplished by inserting a lance through the upper furnace and injecting air through that lance. OFA provides modest NO_X reductions in the range of 20%. This reduction must be balanced with the cost of additional air handling equipment and the increase in unburned carbon and CO emissions.

Approaches for OFA include *Advanced OFA,* which involves injecting air at higher velocities to obtain more mixing in the combustion zone. Additional fan power is required to achieve the higher air velocities. *Separated OFA* involves the installation of air injection ports at a considerable distance above the burners as illustrated in the left side of Figure 6-4. The approach requires that adequate burnout time (i.e., residence time) be maintained after the air is injected.

A practical consideration in using OFA is that boiler tube corrosion may occur in the fuel-rich zone due to the reducing environment in the lower furnace of the boiler. This problem is particularly common in boilers using sulfur-containing fuels. Furthermore, as the stoichiometric ratio is reduced this problem can become very severe.

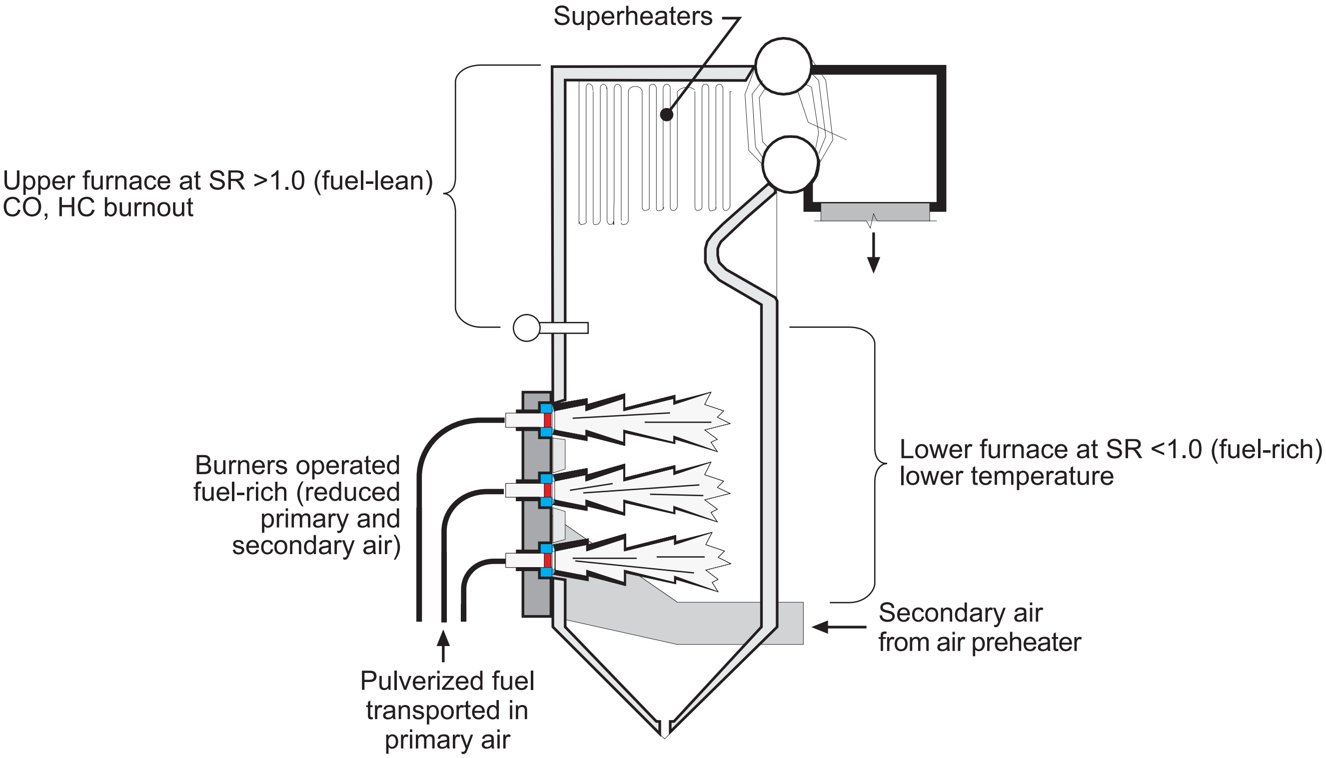


Figure 6-5. Off-stoichiometric combustion

Figure 6-5 demonstrates the operating principles of the OFA method. A secondary air port or OFA injection port has been added above the primary air-fuel burner. Below this port is the fuel-rich zone (stoichiometric ratio less than 1) with peak temperatures lower than those associated with conventional combustion (stoichiometric ratio greater than 1). The injection of OFA allows the upper zone of the furnace to achieve a stoichiometric ratio greater than 1 (fuel-lean) and promotes the burnout of CO and hydrocarbons. If the secondary air ports are located too far from the burners, the residence time will be inadequate to allow for burnout of the CO and hydrocarbons.

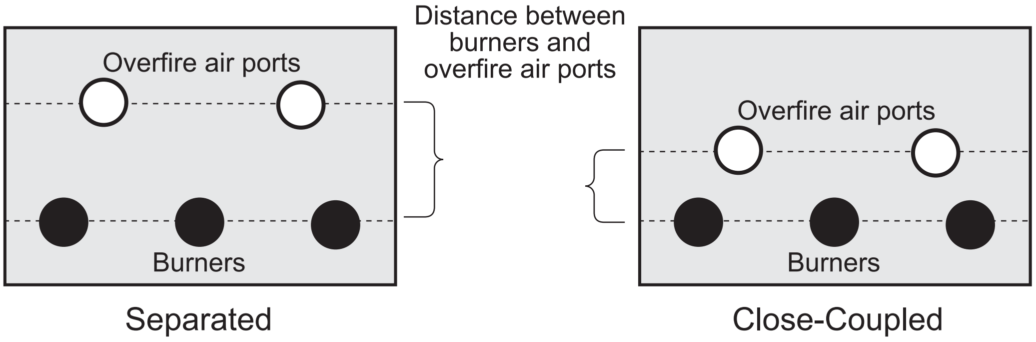


Figure 6-6. Close-coupled and separated overfire air

Figure 6-6 schematically demonstrates the difference *between close-coupled OFA* (CCOFA) and *separated OFA* (SOFA). CCOFA is the conventional OFA technique that is distinguished from SOFA by the location of the OFA ports to the burners.

The SOFA technique is illustrated on the left side of Figure 6-6, while CCOFA is illustrated on the right side of Figure 6-6. SOFA imposes a greater distance between the burners and the OFA ports than the CCOFA method does. In CCOFA the overfire air ports can be located relatively close to the burners. CCOFA reduces the residence time in the fuel-rich zone, but increases the residence time in the fuel-lean or burnout zone.

Close-coupled and separated overfire air ports can also be installed on tangentially-fired boilers, although the configuration is different. Figure 6-7 shows the top view of a tangentially-fired boiler. The fuel and air are injected at the corners to create a swirling flame in the middle of the boiler. This is accomplished with a tower of fuel and air ports in each corner of the boiler. A profile of the primary burners and the OFA ports is shown on the left side of Figure 6-7 for SOFA and on the right side for CCOFA. With CCOFA, the close proximity of the OFA ports to the burners can be seen, while the SOFA method provides a distinct physical separation between the OFA ports and the burners. The SOFA method provides additional residence time in the fuel-rich zone and less residence time in the burnout zone.

Figure 6-8 shows the configuration of the use of OFA in a stoker grate boiler. In normal operation, the undergrate air is fed underneath the fuel bed to maintain combustion on the bed. The upper grate air has been traditionally used for burnout. In NO_X control using OFA, some of the undergrate air and/or the upper grate air are diverted to the OFA port. The gases coming off the bed are incomplete combustion products. The OFA provides for a fuel-lean zone that can complete burnout of the combustion products.

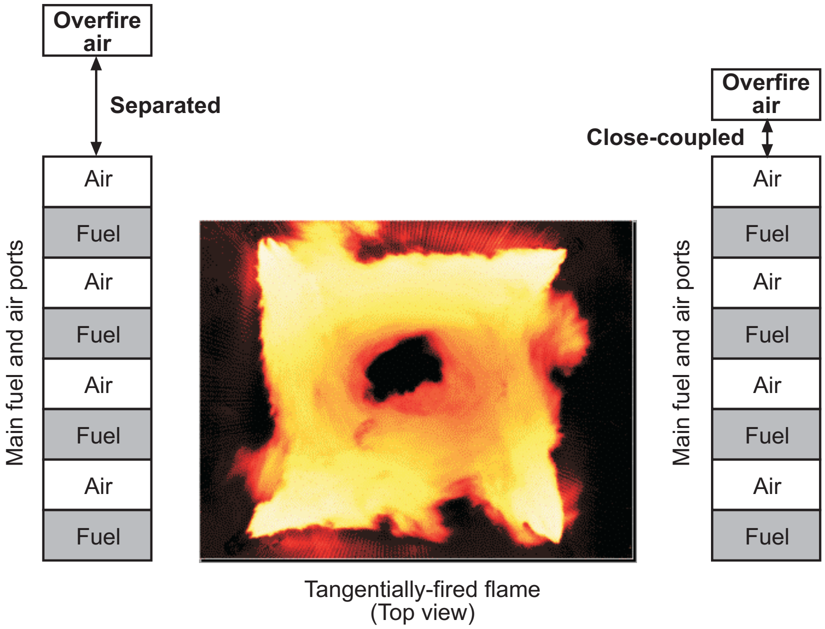


Figure 6-7. Overfire air port arrangements

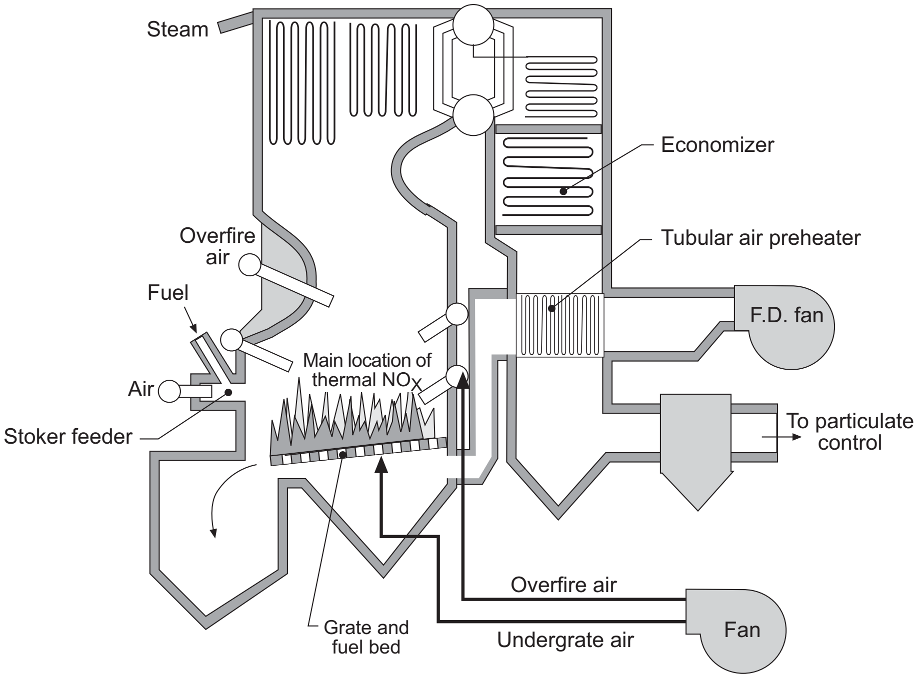


Figure 6-8. OFA arrangement in a stoker-grate boiler

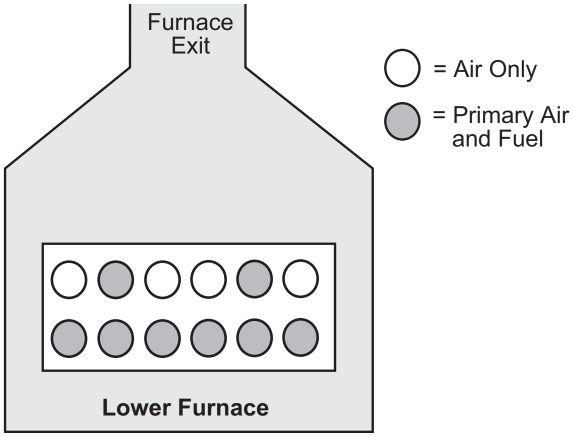


Figure 6-9. Burner firing condition using burners-out-of-service approach

OFA is not highly effective when applied to spreader stoker boilers, overfeed stokers, and undergrate stokers. In these types of boilers, combustion occurs on the grate surface and the units are already equipped with overfire air systems. Additional air ducts above the grate and additional overfire air flow do not significantly reduce the NO_X emission levels.

Burners-Out-Of-Service

When some burners are operated on air only, this modification is called burners-out-of-service (BOOS), as shown in Figure 6-9. Burners out of service is typically performed with no more than 25% to 30% of the burners.[5]

BOOS is similar to OFA, but does not require the installation of new OFA ports. The approach is to reduce air to several of the lower burners and to eliminate fuel in several upper level burners. This arrangement simulates an OFA air system because the reduced air in the lower burners creates a fuel-rich zone and the reduction of fuel in the upper ports creates a fuel-lean zone.

Using BOOS on an existing boiler can result in a steam load reduction if the active fuel burners do not have the capacity to supply fuel for a full load. Therefore, BOOS is typically used on wall-fired units and other units that have the ability to operate at less than full load conditions.

Most utility boilers installed since 1971 have been designed with overfire air ports so that all fuel burners are active during the staged combustion operation.[6] Using staged combustion modifications on oil- and gas-fired boilers reduces NO_X emissions by approximately 30% to 40%.[6] Modifying existing coal boilers has reduced NO_X emissions 30% to 50%.[3]

Staged combustion can also be accomplished by careful control of air and fuel mixing in the burner.

Biased Firing

In some boilers, a number of the burners are operated fuel-rich, and others are operated air-rich in a staggered configuration called biased firing, as shown in Figure 6-10. Rather than use some burners exclusively for air flow (as is done in BOOS), bias firing involves adjusting the stoichiometry in each burner by reducing combustion air in some burners and increasing combustion air flow to other burners. Fuel flow to all burners is maintained so that the stoichiometry ratio varies among burners, but an adequate overall stoichiometry is maintained. This approach decreases the peak flame temperature, similar to BOOS. However, because all burners are firing air and fuel in biased firing, there is less load penalty.

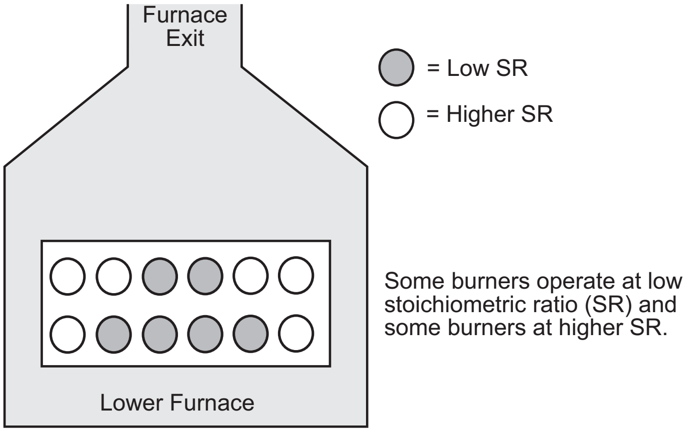


Figure 6-10. Burner firing conditions using the biased firing approach

Practical Considerations of Off-Stoichiometric Combustion

A number of practical considerations exist in using off-stoichiometric firing techniques to reduce NO_X emissions. This is particularly true of older units, where it may be difficult to identify locations for the installation of the OFA ports. For example, furnace volume can be an issue from the standpoint of having enough overall volume in the boiler to ensure adequate burnout.

Fan capacity can be another issue resulting from the use of OFA. A fan is required that can generate a high pressure drop to inject the combustion air into the flue gas stream. Inadequate velocity will cause inadequate mixing in the unit and produce high amounts of unburned hydrocarbons and CO.

Another concern is the extent to which the boiler control system must be modified in order to control critical parameters. Controlling the different amounts of fuel and air that are required to be delivered to the burners and controlling OFA dampers may require substantial installations of equipment. Air infiltration can cause problems in controlling the amount of O_2 that is entering the boiler system. The ability to control air flow at both high and low load conditions and the ability to physically locate new air ducts on the outside of the unit are major factors in deciding if an OFA approach is appropriate for reducing NO_X emissions, particularly in older units. Air infiltration problems in older boilers can also complicate the achievement of appropriate overfire air conditions.

Finally, flue gas residence time is another major consideration in using off-stoichiometric firing, particularly OFA. Specifically, the temperature and the amount of time between the injection of the primary air and the OFA must be adequate for complete burnout.

6.2.3 Flue Gas Recirculation

Flue gas recirculation (FGR) has been used to reduce thermal NO_X emissions from large coal-, oil-, and gas-fired boilers. A portion (10% to 30%) of the flue gas exhaust is recycled back into the main combustion chamber by removing it from the effluent gas stream and mixing it with the secondary air entering the windbox that supplies the burners (Figure 6-11).

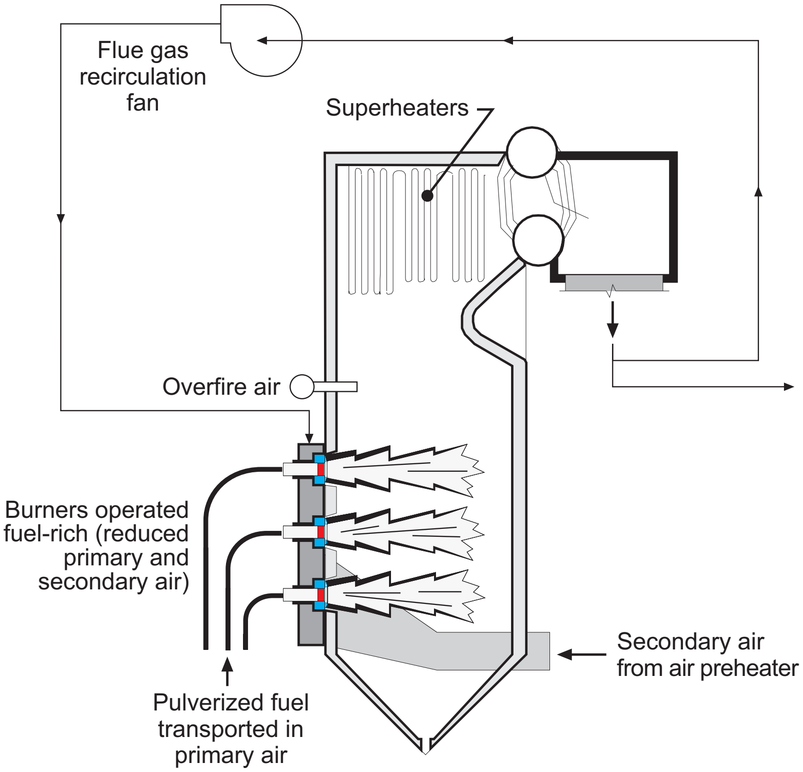


Figure 6-11. Flue gas recirculation

This recirculated gas lowers the flame temperature and dilutes the oxygen content of the combustion air, thus lowering NO_X emissions. NO_X reductions of 15% are typical with flue gas recirculation.

However, NO_X reduction of approximately 40% to 50% is possible with recirculation of 20% to 30% of the exhaust gas in gas- and oil-fired boilers. At high rates of recirculation (e.g., 30%), the flame can become unstable, increasing carbon monoxide and partially oxidized organic compound emissions.

FGR requires greater capital expenditures than low excess air and staged combustion modifications. High temperature fans (forced or induced draft) ducts, and large spaces are required for recirculating the gas.

FGR can be used with OFA techniques to achieve even greater reductions in NO_X emissions. FGR can also be conducted internally when used in conjunction with new, advanced burners. Internal FGR recirculates the flue gas by means of aerodynamic forces instead of the recirculating flue gas fan that is used with conventional FGR.

Some operational problems can occur using FGR. Limited applicability of FGR can be caused by flame instability, loss of heat exchanger efficiency, and condensation of partially oxidized compounds on internal heat transfer surfaces.[6]

6.2.4 Reduced Air Preheat

Reduced air preheat decreases the combustion air temperature by having a portion of the incoming combustion bypass the air preheater (Figure 6-12). By lowering the temperature of the secondary combustion air, the combustion zone peak temperature is reduced.

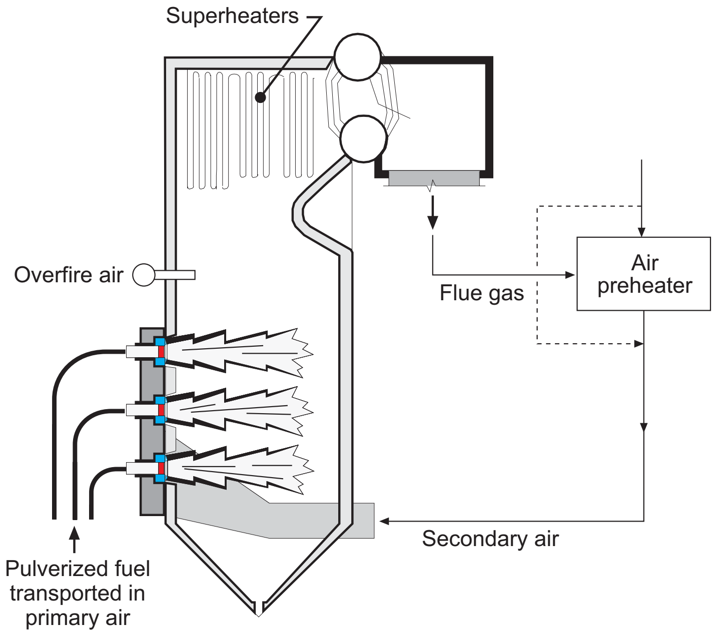


Figure 6-12. Reduced air preheat

Since reduced air preheat is based on reducing the peak combustion temperature, it is most effective in reducing thermal NO_X. This technique is limited to sources that fire low nitrogen fuels, because fuel NO_X is not reduced.

Reduced air preheat creates a trade-off between NO_X reduction and boiler efficiency. When the air bypasses the air preheater, it increases the stack gas temperature and thus decreases the boiler efficiency.

Reduced air preheat can also have beneficial operating and maintenance effects for some types of stokers firing coal with low ash fusion temperatures. The reduced air preheat can be used as a portion of the underfire air, and thus reduce the temperature of the underfire air. This reduction in underfire air temperature could help prevent ash fusion on the grate.

6.3. SUMMARY

A summary of the advantages and limitations of common combustion modification techniques is provided in Table 6-1. However, in reviewing this comparative information, it is important to note that the applicability and effectiveness of combustion modifications is highly specific to combustion systems and sites.

Table 6-1.
Summary of Combustion Modification Advantages and Disadvantages [5,6,7,8]

Technique	Procedure	Advantages	Disadvantages	Percent Reduction		Applicability
LEA	Decreases amount of oxygen available for combustion	Improves efficiency Only combustion controls need modification	Low NOx reduction	Gas	16-20	All fuels
				Oil	16-20	
				Coal	20	
Off-Stoichiometric a. OFA b. BOOS c. Biased Firing	Staged Combustion	a. Compatible with other techniques b. Low capital cost c. Low capital cost	a. High capital cost (retrofit-port installation)	Gas	30-40	All fuels
				Oil	30-40	
				Coal	30-50	
FGR	Recirculate flue gas (<30%)	Potential for significant NO_X reductions	Flame instability High capital costs	Gas	40-50	Low nitrogen fuels
				Oil	40-50	
				Coal	NA	
Reduced Air Preheat (RAP)	Portion of combustion air is not preheated	Potential for significant NO_X reduction	Decreased efficiency	Gas	15-25	Low nitrogen fuels
				Oil	15-25	
				Coal	15-25	

Combustion system modifications will continue to be an important component of the overall NO_X control strategies used by a wide variety of combustion sources.

Review Exercises

1. What factors limit the effectiveness of combustion modifications to suppress NO_X formation?
   a. Carbon monoxide formation
   b. Increased combustible levels in fly ash
   c. Boiler tube fouling
   d. N_2O formation
   e. All of the above

2. What happens to the stack gas temperature when the amount of reduced air preheat increases from 20% to 30%?
   a. Decreases
   b. Increases
   c. Remains the same

3. What factors influence the excess air rate in a boiler?
   a. Fuel-air ratio set by the boiler controller
   b. Air infiltration into the boiler
   c. Air infiltration into the air preheater
   d. All of the above

4. Select all of the effects that result when excess air is increased.
   a. Decreased NO_X emissions
   b. Increased stack gas temperature
   c. Decreased boiler efficiency

5. What is the primary objective of flue gas recirculation systems?
   a. Burn as much as possible of the fuel under fuel-rich conditions where the peak gas temperature and the peak oxygen concentrations are at a minimum
   b. Generate CO to serve as a reducing agent for NO_X compounds
   c. Minimize the peak oxygen level in the combustion zone

6. Which combustion modification technique should be performed prior to any others to establish baseline NO_X data?
   a. Flue gas recirculation
   b. Burner-out-of-service
   c. Low excess air
   d. Reduced air preheater

7. Which of the following combustion modifications could possibly require a reduction in load?
   a. Burners-out-of-service
   b. Flue gas recirculation
   c. Biased burner firing

d. Overfire air

8. Which of the following combustion modifications are less effective at reducing NO_X when high nitrogen fuels are fired?
   a. Overfire air
   b. Burner-out-of-service
   c. Reduced air preheat
   d. Flue gas recirculation

9. Burners-out-of-service generally don't operate with more than ___ % burners-out-of-service.
   a. 25% to 30%
   b. 5% to 10%
   c. 45%% to 55%
   d. 75% to 80%

10. Which of the following pollutants remains at a low level when either insufficient or excessive amounts of excess air are present?
    a. Nitrogen oxides
    b. Carbon monoxide
    c. Particulate
    d. All of the above

References

---

[1] Code of Federal Regulations 40, Part 60, Method 3B, revised July 1, 1997.

[2] Dukelow, Sam G., 1991. *The Control of Boilers*, The Instrument Society of America, 2nd Edition.

[3] Payne, William F., and Richard E. Thompson. 1996. *Efficient Boiler Operations Sourcebook.* The Fairmont Press, Inc.

[4] Vatsky, J. October 7-10, 1991. *Field Experience in Over 7,000 Mwe of Low* NO_X *Burner Retrofits.* Presented at the Joint Power Generation Conference. San Diego, CA.

[5] U.S. Environmental Protection Agency. Office of Air Quality Planning Standards. February 1992. *Summary of* NO_X *Control Technologies and Their Availability and Extent of Application.* EPA-450/3-92-004.

[6] U.S. Environmental Protection Agency, Office of Air Quality Planning Standards. January 1983. *Control Techniques for Nitrogen Oxides Emissions from Stationary Sources.* Revised Second Edition. EPA-450/3-83-002.

[7] Clapsaddle, C.A., and M.A. Acree. June 19-24, 1994. *Development of a Parametric* NO_X *Emission Estimation Correlation for Oil- and Gas-Fired Boilers.* Paper 94-TP29B.05. Presented at the 87th Annual Meeting of the Air and Waste Management Association. Cincinnati, OH.

[8] U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. November 1999. *Nitrogen Oxides (*NO_X*), Why and How They Are Controlled.* EPA-456/F-99-006R.

7 Low NO_x Burners

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. State the two general principles that low NO_X burners (LNBs) implement to reduce NO_X formation.
2. Describe the three parameters that LNBs manipulate to reduce NO_X formation.
3. Identify the degree of NO_X reduction that can be achieved by LNBs and the factors that influence the reduction.
4. Discuss the flame characteristics of staged air burners as they relate to NO_X formation.
5. Describe how staged air burners and staged fuel burners handle combustion air differently
6. Discuss the operational issues that may arise as a result of LNB technology.

7 Low NO_x Burners

Low NO_x burners (LNBs) were originally developed in the 1970s. They were first used commercially in the early 1980s and are now used extensively on a major fraction of industrial and utility boilers. They come in a variety of designs and can be retrofitted to most coal-, oil-, and gas-fired wall-fired and tangentially-fired boilers. Because of stringent regulatory restraints LNBs are now standard in new boiler designs for EGUs.

Although designs differ, all LNBs control the mixing of fuel and air in a pattern that keeps the flame temperature low and dissipates the heat quickly. LNBs incorporate a combination of some or all of the following NO_x combustion control techniques in a single burner:

- Low excess air
- Off-stoichiometric combustion
- Combustion gas recirculation

Precise flow control of the air and fuel is necessary for optimal efficiency of LNBs. The burner management system and the air flow dampers on retrofitted units must to be updated if not adequate.

This chapter addresses the operating principles for LNBs and provides some information on basic design principles for both wall-fired and tangentially-fired boilers. Lastly, this chapter addresses some operational issues associated with the use of LNBs.

7.1 LNB OPERATING PRINCIPLES

The operating principle behind LNBs is to maintain adequate combustion process efficiency, which means having good *burnout* (or complete combustion of the fuel), a stable flame, and stable operation of the burner. NO_X control in LNBs is based on the same principles as the combustion modification technique of over-fired air (OFA) and staging. In general, this means maintaining a lower flame temperature and staged mixing of the fuel and air.

Maintaining combustion efficiency and reducing the formation of NO_X are often in conflict. For example, the mixing of fuel and air must be rapid to ensure good combustion, but it must be slow to minimize the formation of NO_X. The same is true for temperature – high temperatures favor good combustion, but high temperatures also favor NO_X formation. The challenge is to balance these factors to obtain both the combustion efficiency and the low NO_X operation that are required.

One method of reducing the formation of NO_X is combustion staging or the use of OFA. In this method the primary fuel-air mixture is burned in the lower burner area of the furnace with a stoichiometric ratio of less than 1. Secondary air or OFA is inserted downstream to complete burnout. This approach results in moderate NO_X reductions.

Another method of reducing the formation of NO_X is flue gas recirculation. In this method flue gas is injected with the primary fuel-air into the burner. Flue gas recirculation may also use secondary air or OFA injection. The purpose of flue gas recirculation is to dilute the fuel-air ratio in the primary flame near the burner and to slightly reduce the peak flame temperature. Both combustion staging and flue gas recirculation are used in designing LNBs.

LNBs apply these principles in a single burner and accomplish the staging and flue gas recirculation by aerodynamic control of the fuel, air, and combustion products in the burner, rather than using a separate port for injection and subsequent mixing.

> LNBs are designed to operate at lower flame temperatures than conventional burners. By staging combustion, the residence time at high temperatures is decreased and residence time at reduced conditions is increased.
>
> Reduced conditions occur in fuel-rich zones where oxygen is limited and temperatures remain low. Residence time is maximized during this condition to allow the volatized fuel-nitrogen compounds to decay without forming NO_X.

A 20% to 50% reduction in NO_X can be expected through the use of LNBs. Reductions will vary depending on the fuel type, burner design, operating practices, and overall fuel-air supply system. Because of the low nitrogen content of natural gas, reductions greater than 20% to 50% can be achieved.

> Manufacturers have documented efficiencies higher than 60% on a few specific units.[1]

Effluent NO_X concentrations less than 10 ppm can be achieved by using natural gas in “ultra” LNBs. However, these “ultra” LNBs require the use of flue gas recirculation, which requires additional fan power. Finally, effluent NO_X concentrations in the 200 to 400 ppm (0.3 lb/MMBtu to 0.55 lb/MMBtu) range can be expected for coal-fired units using LNBs.

For additional emissions control, LNBs are often applied in conjunction with overfire air (OFA). NO_x levels of 0.21 lb/MMBtu have been demonstrated with OFA compared with 0.30 lb/MMBtu to 0.50 lb/MMBtu with LNBs alone.[2]

7.2 WALL-FIRED LNBs

LNBs have been developed by a large number of manufacturers to reduce NO_X emissions. Although LNB designs may vary, their fundamental NO_X control methodologies are similar. The general burner design and a few specific examples for wall-fired units are provided in this section.

The basic LNB designs for wall-fired units can be divided into staged air burners and fuel staged burners. Staged air burners are designed to control the flame shape in order to minimize the reaction of nitrogen and oxygen at peak flame temperatures. Staged fuel designs burn fuel-lean in the primary zone and fuel-rich in the secondary zone. The reduced flame temperature and combustion gas recirculation suppress NO_X formation for staged fuel LNBs.

7.2.1 Staged Air Burners

Staged air is an early LNB design that employs staged air within the burner.

A general staged air burner design is shown in Figure 7-1. This is a wall-fired burner (also called a *dual register burner*) where, in the first stage, fuel and primary air enter through the center tube of the burner. There may also be swirl vanes in the primary fuel zone to control fuel flow.

The fuel-air mixture is injected into the burner to create a fuel-rich axial flame core in the primary combustion zone of the burner.

The temperatures of flames in the fuel-rich zone are kept low due to the sub-stoichiometric conditions. A short residence time is established in the primary zone in order to delay combustion of the fuel. Fuel NO_X formation is reduced by limiting the available oxygen in the initial combustion zone. Because of the lack of oxygen,n intermediate compounds of nitrogen decay to form molecular nitrogen instead of NO_X.

For low NO_X operation, secondary air or staged air must be added so that the mixing of secondary air is slower than with conventional non-LNBs. The fuel-air mixing in a non-LNB is very rapid and turbulent. This creates a combustion environment with a stoichiometric ratio greater than 1 (fuel-lean). In an LNB, secondary air is injected into a fuel-rich flame. The secondary air will usually travel in a separate annular region around the primary fuel.

This creates a field of air surrounding the fuel-rich flame that gradually mixes with the partially burned products. The effect is a lower flame temperature that results in lower NO_X formation. This technique may also lengthen the flame, which restricts the size of unit in which LNBs can be retrofitted.

> However, the elongated flame allows for radiational cooling, which is beneficial for thermal NO_X reduction. Since fuel NO_X formation is limited in the primary zones, staged air burners are beneficial for nitrogen-containing fuels.

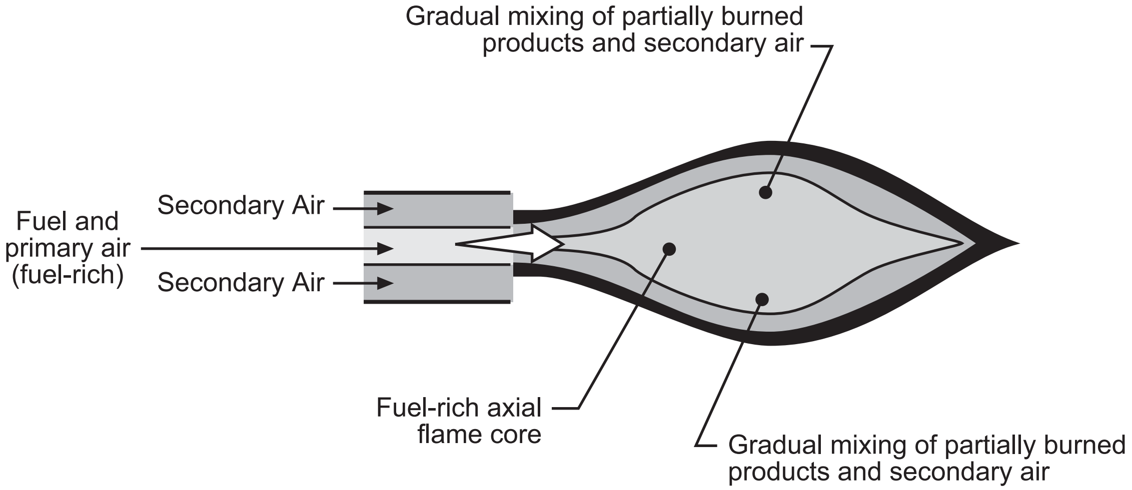


Figure 7-1. Staged air burner

Another method used to control the flame is to add swirl near the burner exit. This can be done with secondary air by creating a recirculation zone in the secondary air flow. Recirculation can lower peak flame temperature, dilute the mixing of fuel and air, and reduce the formation of NO_X in the flame.

A number of LNB designs, typical of coal designs, currently exist on the market. Each manufacturer has a different approach for reducing mixing, while maintaining a fuel-rich axial flame as well as flame stability. A major obstacle in the development of LNBs was maintaining flame stability, which is a key feature of an LNB.

Dual Register Low NO_X Burners

One example of a staged-air burner design is the dual register low NO_X burner by Babcock & Wilcox (shown in Figure 7-2). The mixture of pulverized coal and primary air is controlled to provide fuel-rich combustion in the primary zone.

The remainder of the combustion air (secondary air) is introduced through two concentric air zones that surround the coal nozzle.

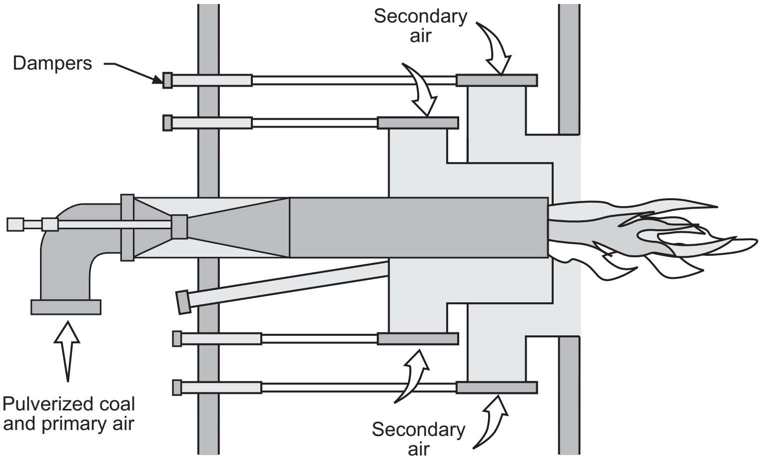


Figure 7-2. A dual register low NO_X burner design

Controlled Flow Split Flame burner

Figure 7-3 displays the flow split flame burner by Foster Wheeler Energy Corporation. The pulverized coal conveyed to the burner by the primary air stream is divided into four concentrated streams.[1] Secondary air is introduced to the annular region of the flame.

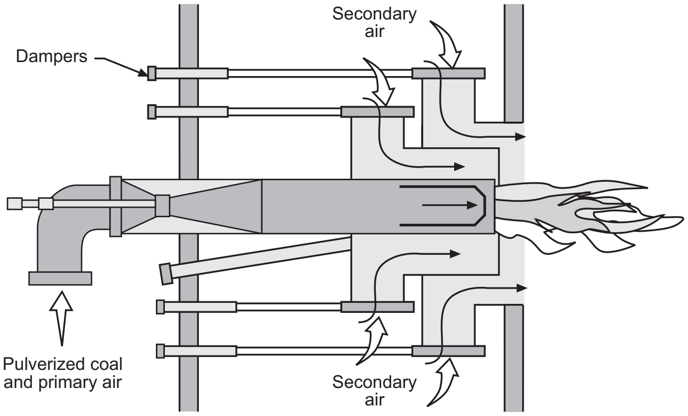


Figure 7-3. Example of a controlled flow split flame low NO_X burner

Distributed Mixing Burner

The distributed mixing burner was designed by EPA and is shown in Figures 7-4 and 7-5. The primary zone is operated fuel-rich with a circular burner. Primary air and fuel are mixed with secondary air with swirl vanes for primary combustion. After a short residence time, combustion is completed with tertiary air injection.

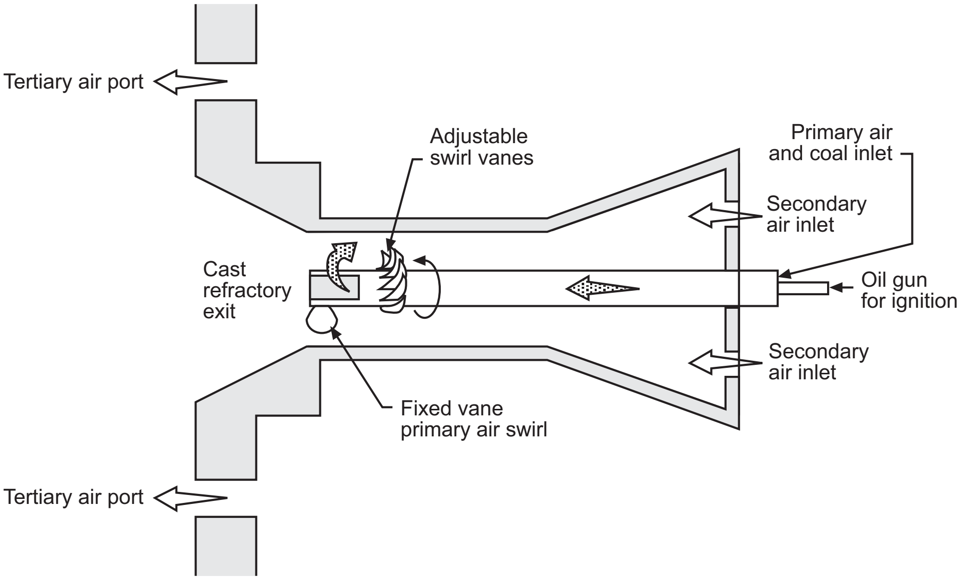


Figure 7-4. Distributed mixing burner[3]

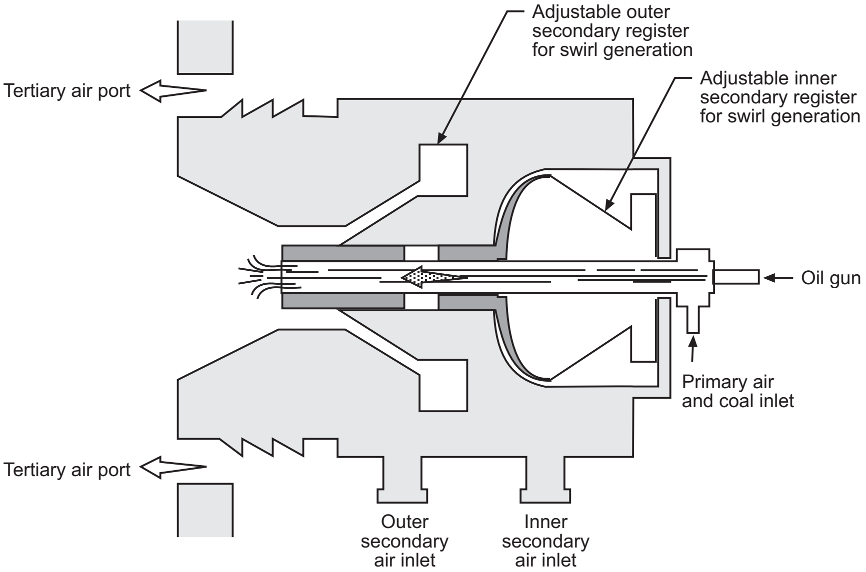


Figure 7-5. Distributed mixing burner[3]

7.2.2 Staged Fuel Burners

Staged fuel burners also use a two-stage design for NO_X reduction (Figure 7-6). Unlike staged air burners, staged fuel burners are only designed for gas firing. A portion of the fuel and *all* of the combustion air are introduced into the primary combustion zone. By operating the primary zone fuel-lean the peak flame temperatures are reduced.

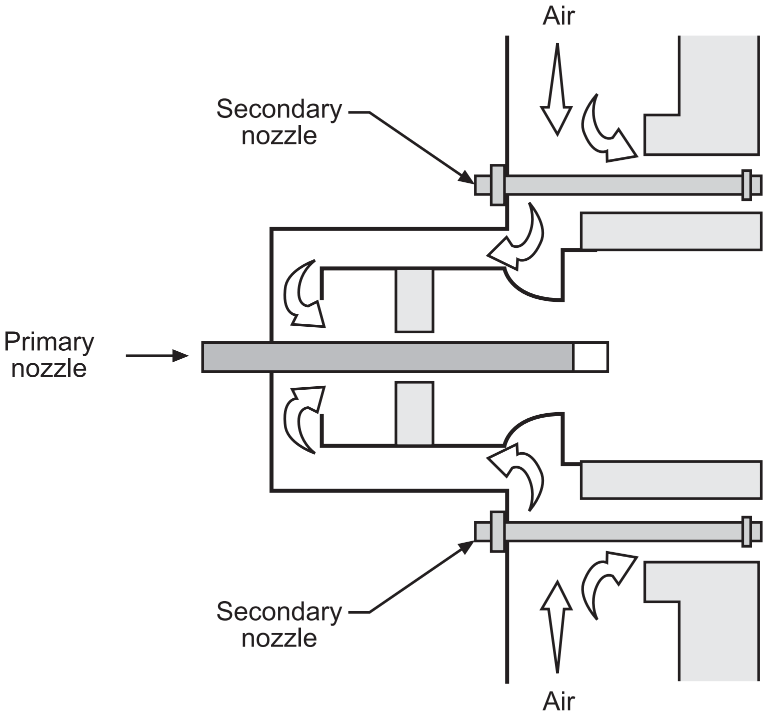


Figure 7-6. Staged fuel burner[2]

The balance of the fuel is introduced through a series of high-pressure nozzles located around the perimeter of the primary combustion zone. The turbulence created by the pressurized fuel injection entrains surrounding flue gas. FGR is accomplished by this rapid mixing of the fuel and surrounding flue gas.

As shown in Figure 7-7, FGR uses an external recirculation zone that is outside the fuel-rich axial flame core and an internal recirculation zone within the fuel-rich zone. This configuration maintains flame stability and assists in moving the combustion products toward the hottest part of the flame.

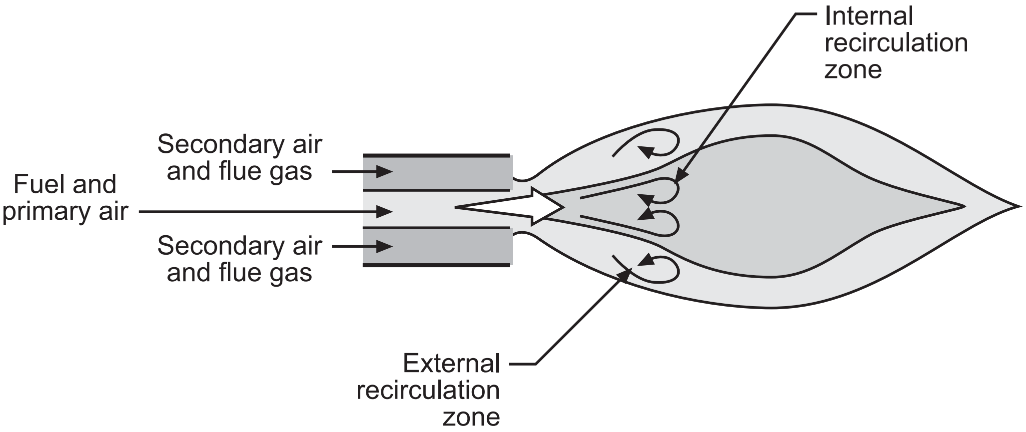


Figure 7-7. Use of flue gas recirculation with LNBs

Staged fuel burners require less excess air than staged air burners. The flame length produced with staged fuel burners is shorter than with staged air burners.

7.3 TANGENTIALLY-FIRED LNBs

LNB designs for tangentially-fired units apply the same principles as those for wall-fired units. This includes staging and recirculation, but using a bulk flame in the furnace as opposed to separate flames associated with individual burners. As a result, LNB designs for tangentially-fired units are less complex than those for wall-fired units. However, the overall system design is at least as complex as a wall-fired unit.

Figure 7-8 shows the top view of the bulk flame in a tangentially-fired LNB. The circled area in the upper left hand corner of the figure is the burner where the fuel and air are injected. On each side of the top view of the flame is a side view showing the inlet ports for fuel and air. On the left is a conventional design showing alternating fuel and air ports, with OFA ports above the top air port. Shown on the right side of Figure 7-8 is the configuration of the fuel and air ports in an LNB system. This LNB configuration creates fuel-rich zones and results in a gradual mixing of fuel and air.

LNBs applied to tangentially-fired boilers create a more distinct separation between the fuel-rich and the fuel-lean zones of the burners than conventional firing. This separation enhances the extent of NO_X control. Changing the supply of fuel or air to the inlet ports as shown in Figure 7-8 creates the distinct zones.

In the LNB design for tangentially-fired units, there is an increase in the distance between the top air port and the OFA port. This is called a *separated air fire* or *advanced OFA system.*

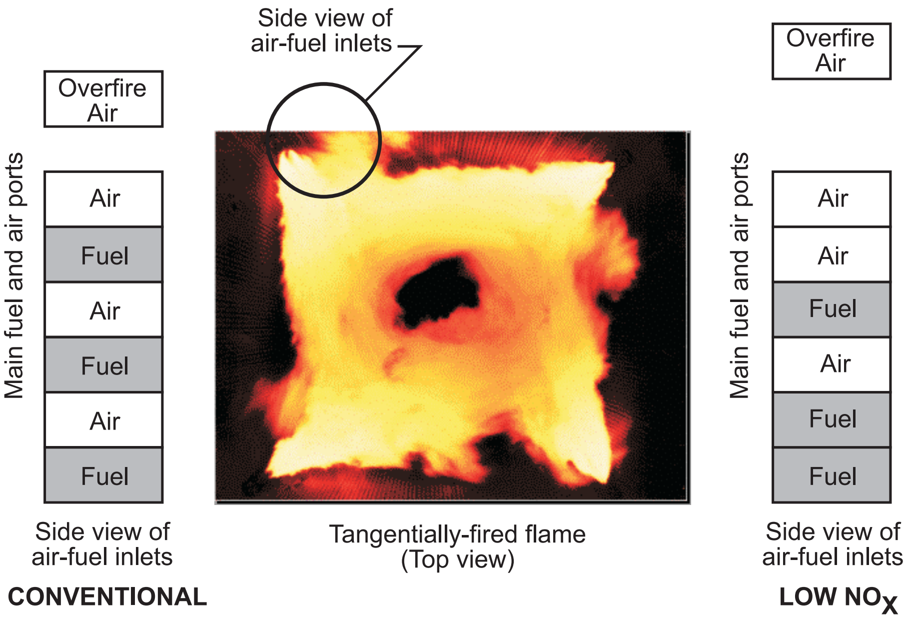


Figure 7-8. Conventional and LNB arrangements for tangentially-fired boilers

Low NO$_X$ Concentric Firing System

In a conventional tangentially-fired unit, the fuel and air are injected at the same angle from the corners of the unit towards the center, creating a tangential swirl as shown in Figure 7-9.

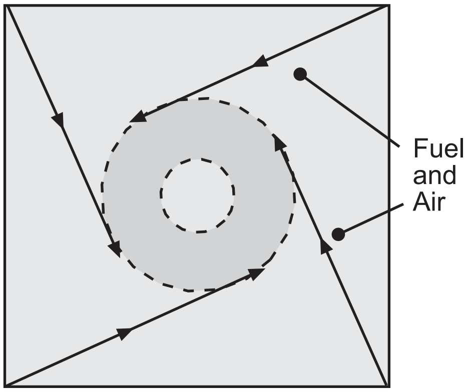


Figure 7-9. Tangentially-fired boiler swirl pattern (conventional)

A low NO_X concentric firing system is shown in Figure 7-10. Primary air and fuel are injected from the burner toward the center of the furnace, while secondary air is added at an angle away from the center. More gradual mixing of fuel and air takes place with a concentric firing system than with a conventional design, which results in lower overall NO_X emissions.

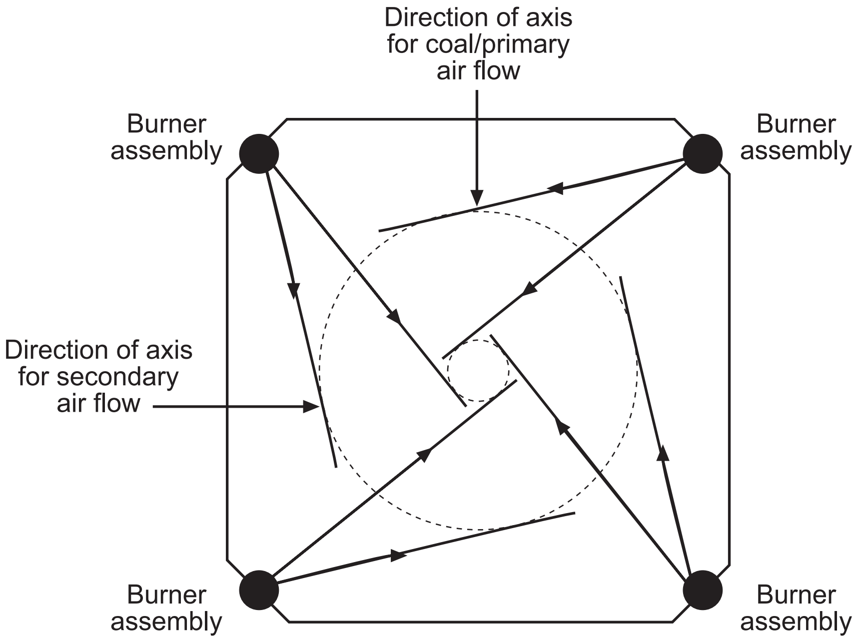


Figure 7-10. Low NO_x concentric firing system[3]

The primary air and fuel stream operates fuel-rich in the primary burn zone. Secondary air is injected to complete combustion in a fuel-lean zone.

More radiant cooling occurs with tangential boilers than with wall-fired boilers. For this reason, tangential boilers have inherently lower thermal NO_X formation.

7.4 OPERATIONAL ISSUES

7.4.1 Applicability

LNBs are applicable to wall-fired and tangentially-fired boilers, but not to cyclone boilers. The Electric Power Research Institute estimates LNBs can be retrofitted on 50% to 80% of existing boilers.[2]

NO_X control efficiency is highly dependent on the specific boiler design and specific LNB model. Proper application of the LNB design depends on many factors, including the following:

- Boiler type
- Boiler size
- Fuel type (e.g., fuel-nitrogen and volatile compounds)
- Existing fuel-air supply system
- Existing burner designs

To an operator, one of most important aspects of LNBs is flame stability. Early models had poor flame stability and were not popular. Improved designs with accurate air-fuel control have offered improved flame stability.

The longer flame created by air staged burners may pose a problem in certain retrofit applications. If the physical dimensions of the combustion chamber are insufficient, the flame may impinge on the boiler wall and derate the boiler (reduce power output).

7.4.2 Flow Control

LNB technology is based on accurately controlling the mixing of fuel and air in a manner that keeps flame temperatures low, heat dissipated, and oxygen supply limited.

The control of burner air-fuel ratios is more critical for LNB than for conventional burners as a result of the need to maintain precise quantities of fuel and air in the fuel-rich flame core and the secondary air. The flow control system must allow the operator to accurately control the air and fuel distribution.

For retrofit applications, some flow control systems may be inadequate, requiring update or replacement.

There is an operating limit on the reduction of flame temperature and staged combustion delay. Lowering the flame temperature and reducing the residence time adversely affects combustion efficiency and stability.

LNB operating control adjustments for efficient combustion are generally opposite of those required for optimal NO_X control. Efficient combustion results in lower CO, lower unburned organic compounds, higher flame temperatures, and improved boiler output. Efficient combustion is also conducive to NO_X formation; therefore an appropriate balance must be achieved by controlling air and fuel flow rates.

Flow control for LNBs is an important part of LNB operation since the low NO_X levels are the result of precise aerodynamic flows of the fuel and air. In order to maintain these flows, it may be necessary to upgrade the burner management system or the flow dampers and actuators. Special difficulties exist with the control of air flow in burner units that have common wind boxes. Use of the common windbox for feeding air and fuel to all boilers creates challenges in balancing the flow among the boilers to ensure that appropriate stoichiometric ratios are achieved.

7.4.3 Unburned Carbon

The use of LNBs may increase the amount of unburned carbon. As the intensity of the flame is reduced, some of the fuel may be lost as unburned carbon. In an oil-fired boiler, this substance is termed *soot* .

Unburned carbon is a consequence of staging and low temperature operation. Unburned carbon, measured as *loss-on-ignition* (LOI), may be reduced by boiler tuning without a substantial increase in NO_X emissions. High LOI has an economic penalty because it results in higher fuel costs: more fuel must be used to obtain the same energy output.

In addition, high LOI levels increase the carbon content in the ash. High ash carbon content may make the ash unsuitable for sale in certain markets (e.g., cement kilns). Reduction in the salability of fly ash and loss of fuel due to unburned carbon increase operating costs.

> Cement and other aggregate manufacturers purchase fly ash for product. Carbon in the fly ash is undesirable and reduces the salability of fly ash. If LOI levels exceed approximately 5%, the quality of the fly ash becomes an issue.

Figure 7-11 shows the inverse relationship between LOI and NO_X emissions. As the figure shows, the LOI levels increase as NO_X emissions decrease.

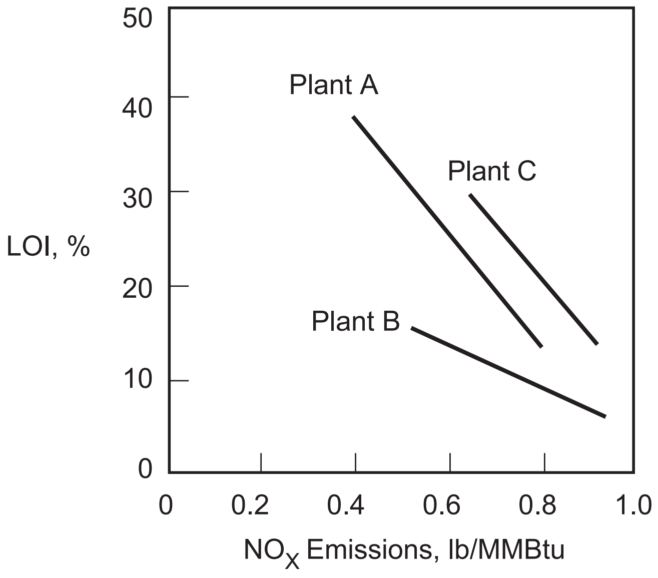


Figure 7-11. Inverse relationship between LOI and NO_X emissions

7.4.4 Boiler Static Pressure Drop

> Swirl vanes or other apparatus are used to control the flow and the mixture of air and fuel. In many designs air is injected in a swirling pattern to form eddies in the burner. These eddies help recirculate combustion products in order to lower peak flame temperatures and limit oxygen availability. However, this swirling action increases the static pressure drop of the boiler.

The increased swirl that results can require larger air flows due to the increased air pressure drop. This results in another economic consequence of using LNBs by requiring the installation of properly sized fans necessary to handle the static pressure drop.

7.4.5 Mechanical Fatigue

Mechanical wear on components is accelerated with use of LBNs. In a coal-fired unit, the coal flows through a small concentric tube into the burner. Poor distribution in the injection ports and tubes results in concentrated streams of coal called *roping*. Coal roping compromises low NO_X formation by preventing a good distribution of the coal into the firing zone. In addition, coal roping can wear flame tips, swirl vanes, and other components.

Adjustments of the air and fuel mixing should be made to prevent roping.

Recent improvements in flame scanners may allow improved performance of LNBs and other combustion modification techniques in the future. Previously, these scanners were used to rapidly shut down fuel flow to a burner in the event that the flame was extinguished. Scanners are also being developed to monitor the average flame intensity, flame ignition point, stability at the ignition point, and size of the fuel stream.[4] These data can be used to optimize the burner performance and to identify burners that are not operating properly.

Review Exercises

1. Why are nitrogen-containing fuels used with staged air burners?
   (Select all that apply.)
   a. The primary zone is fuel-lean.
   b. The primary zone is fuel-rich.
   c. Oxygen is limited in the primary zone.
   d. Oxygen is limited in the secondary zone.
   e. None of the above

2. What is the best choice for a small gas-fired boiler?
   (Select all that apply.)
   a. Controlled flow split burner
   b. Dual register LNB
   c. Distributed mixing burner
   d. Directional flame burner
   e. None of the above

3. What are the techniques applied for controlling NO_X with the staged fuel burner design?
   (Select all that apply.)
   a. Reducing the peak flame temperature
   b. Increasing the residence time at reduced conditions
   c. Recirculating the flue gas
   d. Limiting the oxygen available during combustion
   e. None of the above

4. Which of the following could result in reduced combustion efficiency?
   (Select all that apply.)
   a. Mixing of the fuel and air in a slow controlled pattern
   b. High LOI levels
   c. High flame temperatures
   d. Recirculation of combustion gases
   e. None of the above

5. What is the typical control efficiency for LNBs?
   a. 75% to 95 %
   b. 50% to 75 %
   c. 20% to 50 %
   d. 5% to 20 %

6. Which of the following produces the shortest flame?
   a. Staged air burner
   b. Staged fuel burner
   c. Tangentially-fired LNB
   d. All are approximately the same.
   e. Depends on the model of low NO_X burner

7. Staged air burner designs may produce a(n) _____________ in comparison to conventional burners?
   (Select all that apply.)
   a. Short wide flame
   b. Elongated flame
   c. Divided flame
   d. Swirling flame
   e. None of the above

8. Swirl vanes are used in certain low NO_X burner designs in order to create eddies in the burner flame. What is the result of these eddies?
   (Select all that apply.)
   a. Recirculation combustion products
   b. A localized reduction of available oxygen
   c. A reduction of the peak flame temperature
   d. Increased static pressure drop of the boiler
   e. None of the above

9. Which of the following techniques reduce NO_X formation with the application of LNBs to tangentially-fired boilers?
   (Select all that apply.)
   a. Pre-mixing of the fuel and air
   b. Addition of swirl vanes
   c. Increased turbulent mixing of air and fuel
   d. Creating a more distinct separation between the fuel-rich and air-rich zones
   e. None of the above

10. Roping is a result of which of the following?
    a. Elongated flames
    b. Poor coal distribution in injection ports and tubes
    c. Swirl vanes
    d. Tangentially-fired burners
    e. None of the above

References

---

[1] Vatsky, J. October 7-10, 1991. *Field Experience in Over 7,000 MWe of Low NO_X Burner Retrofits.* Presented at the Joint Power Generation Conference. San Diego, CA.

[2] U.S. Environmental Protection Agency. February 1992. *Summary of NO_X Control Technologies and their Availability and Extent of Application.* EPA-450/3-92-004.

[3] U.S. Environmental Protection Agency. July 1986. *Nitrogen Oxides Control for Stationary Combustion Sources.* EPA/625/5-86/020.

[4] Collins, S. October 1993. *Advanced Flame Monitors Take on Combustion Control.* Power.

8 NO_X Reburning

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Explain the principles of reburning and name two source categories where it is currently applied.
2. Briefly describe combustion conditions in the primary, reburn, and burnout zones and how they result in lowering NO_X emissions.
3. State the requirements for good reburn fuels and name at least five appropriate reburn fuels.
4. State the relationship of the stoichiometric ratio to NO_X emissions.
5. Identify at least three disadvantages or limitations of reburn technology as a stand-alone technology for NO_X control.

8 NO_X Reburning

8.1 INTRODUCTION

Reburning is a NO_X staged combustion control technique that suppresses the formation of NO_X in burners and then provides for additional NO_x reduction in the furnace area of the boiler

The technology was conceived by Dr. Yost Weant, now with the University of Arizona. He applied the reburning concept on a bench scale in the late 1960s. Based on his work, he developed the process and presented a paper in 1973 at the Combustion Institute.

Reburning was first laboratory-tested in the mid 1970s by the Shell Development Company.[1]

Some Japanese researchers applied the concept to bench scale and pilot scale boilers and presented the results of their research at an information exchange conference in Tokyo in 1981.

In the mid-1980s, reburn technology was applied commercially on large-scale boilers in Japan.

At the same time EPA began conducting in-house research on reburn technology, primarily focusing on oil and gas as reburn fuels. Later, EPA funded extramural research on the use of coal as a reburn fuel.

Reburning technology is now in use in the U.S., Europe, and Japan for electric generating units and some municipal waste incinerators. NO_x reburning is also called *reburn, in-furnace NO_X reduction*, and *staged fuel injection.*

Reburning is applicable to most types of boilers, including cyclone-fired boilers. NO_X reductions of 50% to 70% at full boiler load have been demonstrated with gas reburning on coal- and oil-fired boilers.[2] In most applications a reduction of more than 60% has been achieved with minimal impacts on boiler performance and durability.[3] Table 8-1 displays reburn performance data for coal-fired boilers in the U.S. as of 1999.[1]

Table 8-1
Reburning Application of Coal-Fired Boilers in the United States[1]

Location	Boiler Type	Capacity (MW)	Reburn Heat (%)	NO_X Emissions (lb/MMBtu)		NO_X Reduction
				Uncontrolled	Controlled	
Gas Reburning						
Hennepin	Tangential	71	18	0.75	0.25	67
Lakeside	Cyclone	33	23	0.97	0.39	60
Cherokee	Wall-Fired	158	18	0.73 (with LNB)♦	0.27	63
Greenidge	Tangential	100	10	0.50	0.25	50
Kodak Park	Cyclone	69	20	1.25	0.56	56
Kodak Park	Cyclone	50	14	1.20	0.51	58
Kodak Park	Cyclone	50	13	1.20	0.51	58
Crane	Tangential	200	N/A	N/A	N/A	N/A
Coal Reburning						
Nelson Dewey	Cyclone	100	25-30	0.82	0.39	52
Milliken	Tangential-Micronized Coal	150	14	0.35	0.25	28
Kodak Park	Cyclone-Micronized Coal	50	17	1.36	0.59	57

♦ LNB = low NO_X burner

Reburning can be used in combination with a number of other NO_x control techniques. Accordingly, reburning is expected to be a popular control technique in the future.

8.2 REBURNING OPERATING PRINCIPLES

The primary combustion zone is operated at reduced fuel firing rates and at normal or slightly reduced excess air rates. Reducing the fuel fired and limiting oxygen availability in the primary zone results in decreased fuel NO_X formation. By operating the primary combustion zone with reduced amounts of excess air, increased levels of unburned hydrocarbons, carbon monoxide and intermediate nitrogen compounds are formed.

Reburning takes advantage of a chemical reaction shown in Figure 8-1. NO_X formed in the primary combustion zone reacts with species such as HCN and NH_3 to create NO and N_2.

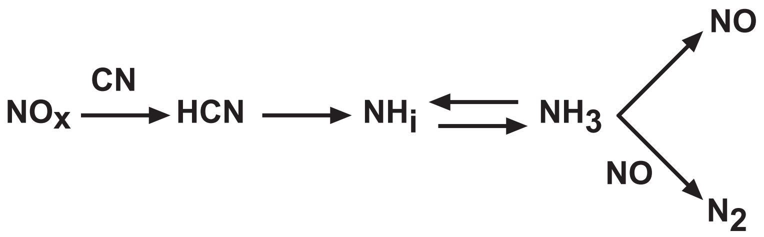


Figure 8-1. Chemical reaction of NO_X in primary combustion zone

The primary combustion zone reactions are represented in a simplified format below.[1]

$$\mathrm{Fuel} + O_2 \longrightarrow CO_2 + CO + H_2O + CN_i + \text{other species} \qquad \text{Reaction 8-1}$$

$$N\,(\mathrm{fuel}) + O_2 \longrightarrow NO_x \qquad \text{Reaction 8-2}$$

$$N_2\,(\mathrm{air}) + O_2 \longrightarrow NO_x \qquad \text{Reaction 8-3}$$

Separate burners are located above the primary combustion zone in the upper portions of the combustion chamber termed the *reburn zone*. The reburn zone is operated under reducing conditions to suppress NO_X formation in the lower array of primary burner flames.

Species such as hydrocarbon radicals (CH_i) are formed in the air-lean reburn zone and react with NO_x formed in the primary combustion zone. Intermediate radicals, such as HCN and amines (NH_i), are formed from this reaction and react under fuel-rich conditions in the reburn zone to form molecular nitrogen (N_2) and water (H_2O). These reactions are represented in Reactions 8-4 through 8-8.[1] The conversion of NO_x to N_2 is dependent on both time and temperature.

$$\text{Reburn fuel} \longrightarrow CH_i + \text{other species} \qquad \text{Reaction 8-4}$$

$$CH_i + NO_x \longrightarrow CN + NH_2 + H_2O \qquad \text{Reaction 8-5}$$

$$NO_x + NH_2 \longrightarrow N_2 + H_2O \qquad \text{Reaction 8-6}$$

$$NO_x + CN \longrightarrow N_2 + CO \qquad \text{Reaction 8-7}$$

$$NO_x + CO \longrightarrow N_2 + CO_2 \qquad \text{Reaction 8-8}$$

Air is injected above the reburn zone so that combustion of the fuel can be completed. This area is termed the *burnout zone*. Any NO_x formation (i.e., thermal NO_x) in the burnout zone is minimal.

The burnout zone reduces unburned hydrocarbons to CO_2 and H_2O and completes oxidation of partially oxidized compounds, as shown in Figure 8-2. A portion of the intermediate nitrogen compounds also converts to NO. The fuel-to-air ratio of the reburn burners can be adjusted to minimize the conversion of intermediate compounds to NO.

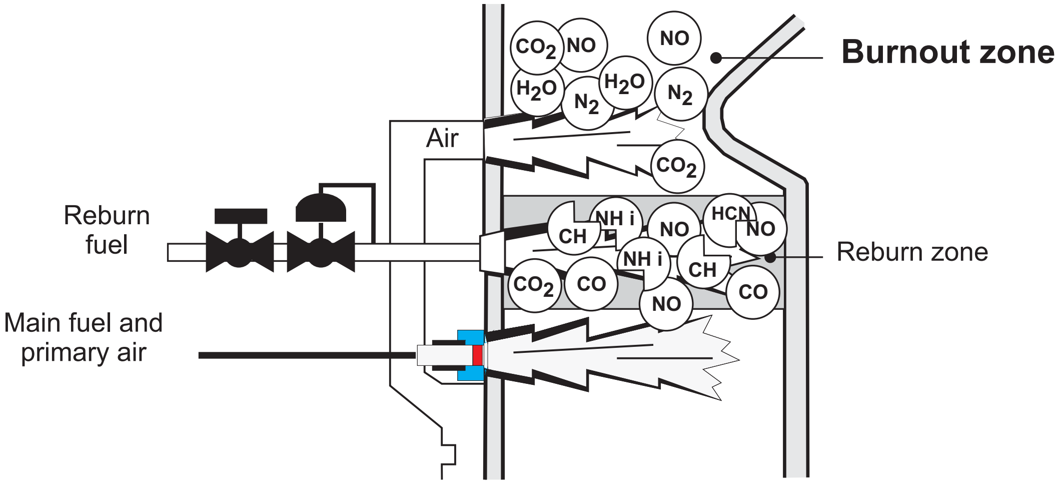


Figure 8-2. Completion of combustion in the burnout zone

The reactions occurring in the burnout zone are represented in Reactions 8-9 and 8-10.[1]

$3O_2 + 2CO + CH_i \longrightarrow 3CO_2 + H_2O$ Reaction 8-9

$CN + NH_2 + O_2 \longrightarrow NO_x + CO_2 + H_2O$ Reaction 8-10

It is apparent that reburning systems incorporate off-stoichiometric firing principles for NO_X emissions reduction.

Reburning fuels include a wide range of hydrocarbon fuels, including the following:

- Natural gas
- No. 2 oil
- Pulverized coal
- Micronized coal
- Emulsified coal
- Processed coal
- Orimulsion™

Natural gas has been the most popular reburn fuel, offering the advantages of burning clean and resulting in low effluent emissions.

In addition, natural gas mixes easily during injection and does not require any preparation prior to use. However, natural gas is often more expensive than the primary fuel and may require the addition of an extensive piping system.

When pulverized coal is used, it is preferable to inject the fuel in a highly atomized condition to ensure a rapid burnout in the boiler and to minimize carbon carryover to the superheated section of the boiler.

This is important since the reburn zone is operated at reduced conditions and provides only a short residence time. Increasing the surface area of fuel provides more rapid burnout and reduction in carryover of carbon to the superheater. Buildup of carbonaceous material on the boiler tubes reduces boiler thermal efficiency and increases ash content.

While the size of oil droplets can be controlled by the method of injection, coal may require treatment prior to injection.

A recent innovation is the use of Orimulsion™ fuel. Orimulsion™ is a fuel produced in Venezuela from a sludge-like hydrocarbon called bitumen.[4]

These reburn fuels can be injected without a supplemental carrier stream or with recirculated flue gas. The reburn fuel is injected in an area of the flue gas stream where temperatures are within 1600°F to 2200°F for efficient NO_X reduction.

8.3 WALL-FIRED REBURNING

Figure 8-3 displays the three separate zones in a wall-fired unit; the primary combustion zone, the reburn zone, and the burnout zone. The *primary combustion zone* is the lower zone. The *reburn zone* is located above the primary combustion zone and is where the reburn fuel is injected into the boiler. The *burnout zone* is above the reburn zone where over-fire air ports add air, allowing complete combustion to occur.

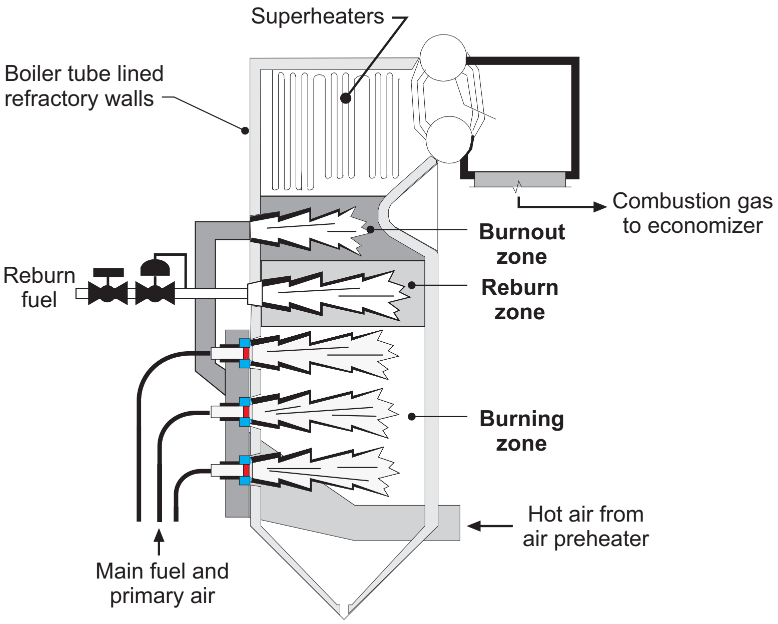


Figure 8-3. Three combustion zones in a wall-fired unit

Primary Combustion Zone

The firing rate in the primary combustion zone (often termed the *burning zone*) is reduced when reburning is used**.**

> When reburning is used, the amount of fuel injected in the primary combustion zone is only 80% to 90% of the fuel injected during operation without reburning.[2] The primary combustion zone is operated with the lowest practical amount of excess air to limit fuel requirements (i.e., 1.1 to 1.2 stoichiometric ratio[1]). By reducing the amount of excess air injected in the primary combustion zone, NO_X formation is reduced and less fuel is required in the reburn zone.

Limiting the fuel injected in the primary zone also results in a reduced firing rate and a lower heat release in the primary combustion zone.

However, 10% to 20% of the boiler heat input is provided in the reburn zone.[2]

The fuel/air stoichiometry is an important operating parameter, and the goal is to add enough fuel to the primary combustion zone to achieve a stoichiometric ratio of 0.9 to 1.0.[5] A stoichiometric ratio closer to 0.9 is preferable.

As shown in Figure 8-1, a number of radicals (e.g., hydrocarbon compounds, NO, NO_2, CO, CO_2) are formed in the primary combustion zone during the combustion process. These radicals would normally be emitted if reburn were not employed.

Reburn Zone

By adding the reburn zone, as shown in Figure 8-4, compounds formed in the primary combustion zone react with the radicals (e.g., amines and hydrocarbon compounds) that are formed by the reducing zone.

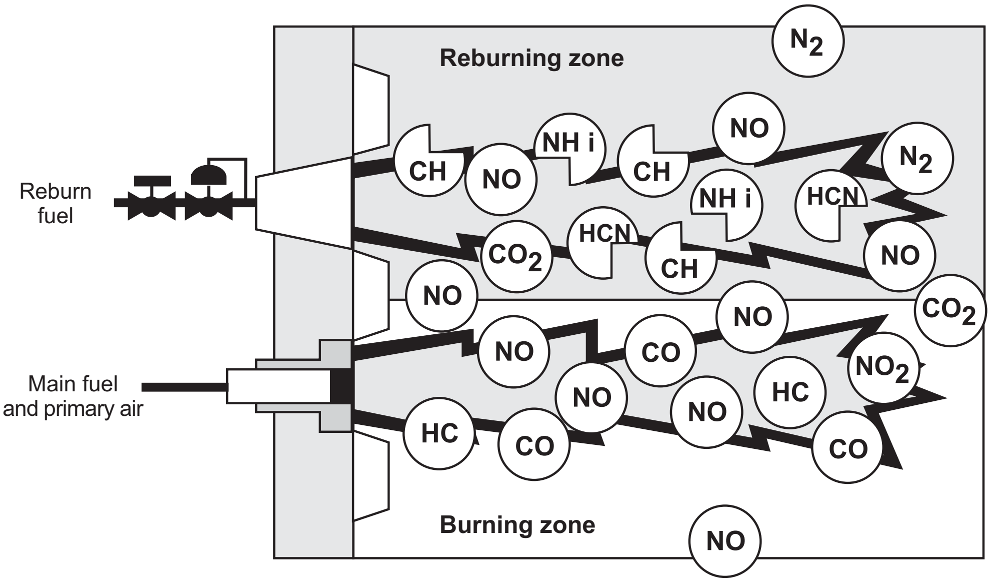


Figure 8-4. Combustion products in the reburn zone

Temperatures in the upper region of the furnace area increase slightly due to the reburning process. This allows for increased heat transfer to the superheaters.[6]

Burnout Zone

Over-fire air is added to the burnout zone where the NO and NO_2 are reduced to N_2 and H_2O. As shown in Figure 8-2, some NO and CO_2 remain in the burnout zone.

Because the primary combustion zone and the reburn zone operate fuel-rich, the burnout zone is necessary to complete combustion of unburned hydrocarbons and partially oxidized compounds. Overfire air ports inject excess air into the burnout zone located above the reburn area. Excess air that is not required for injection in the primary zone can be directed to the overfire air ports.

8.4 CYCLONE BOILER REBURNING

Cyclone boilers operate at high combustion zone temperatures and are designed for poor quality coal. Cyclone boilers allow for slag removal from the bottom of the boiler, thereby reducing particulate matter emissions from the boiler.

Slag is fused or re-solidified molten material in the combustion area.

However, cyclone burners must operate at elevated temperatures in order to maintain slag deposit removal. These conditions are ideal for thermal NO_X formation. Figure 8-5 is a schematic diagram of a cyclone boiler.

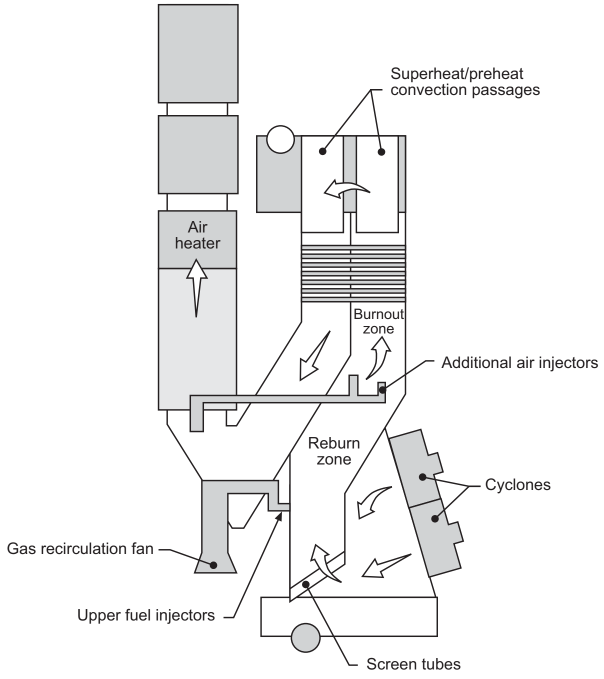


Figure 8-5. Cyclone boiler schematic

NO_X reburning can be used on a cyclone boiler to reduce NO_X emissions.

> Other in-furnace control techniques are either quite costly or not applicable to cyclone burners. Reburning is attractive for cyclone boiler operators because there are few other options available.

Reburning applied to cyclone boilers is similar to wall-fired units. 70% to 90% of the normal amount of fuel is fired in the primary combustion area. The remaining 10% to 30% of the fuel is burned in the reburn area, as shown in Figure 8-6.[1]

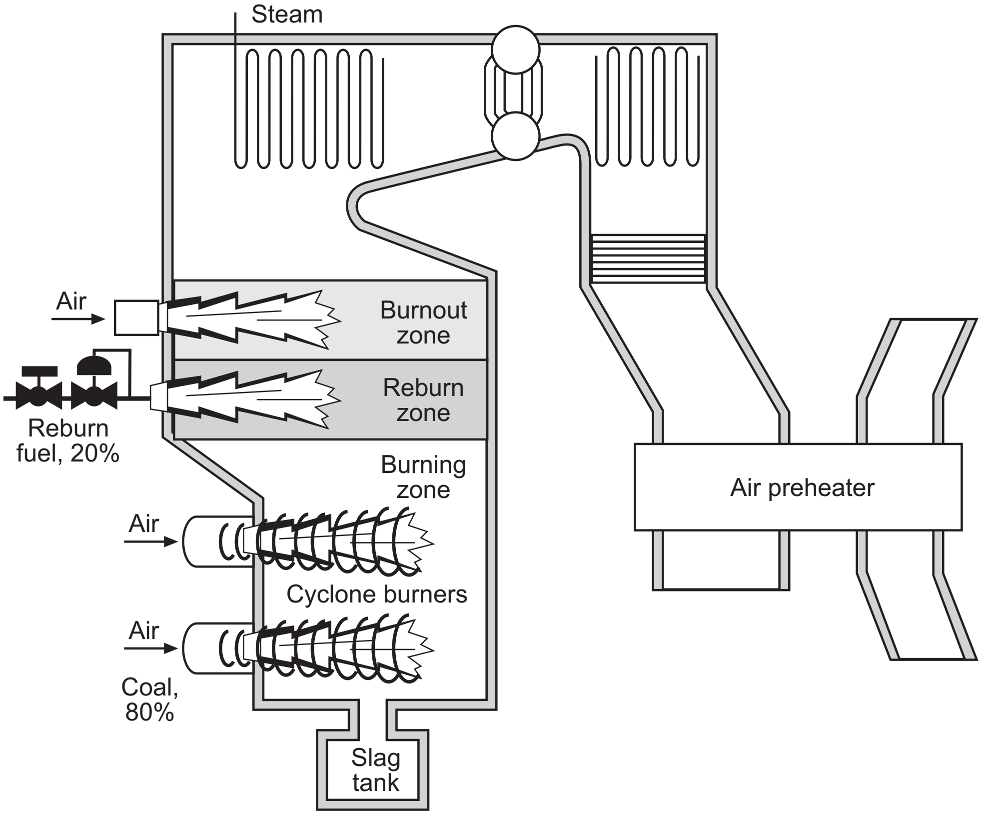


Figure 8-6. Cyclone boiler reburn system

Selection of the fuel (coal, oil, or natural gas) to be used as the reburn fuel depends on the availability and cost of the fuel. Because of variability in both the availability and the cost of reburn fuels, EPA is developing a multi-fuel reburn system capable of switching from one fuel to another.

> Coarse-grade coal burned as the primary fuel does not serve well as a reburn fuel. Large fuel particles reduce interaction in the reburn zone and retard control efficiency. The coal must be pretreated to increase the particle surface area for use as a reburn fuel.

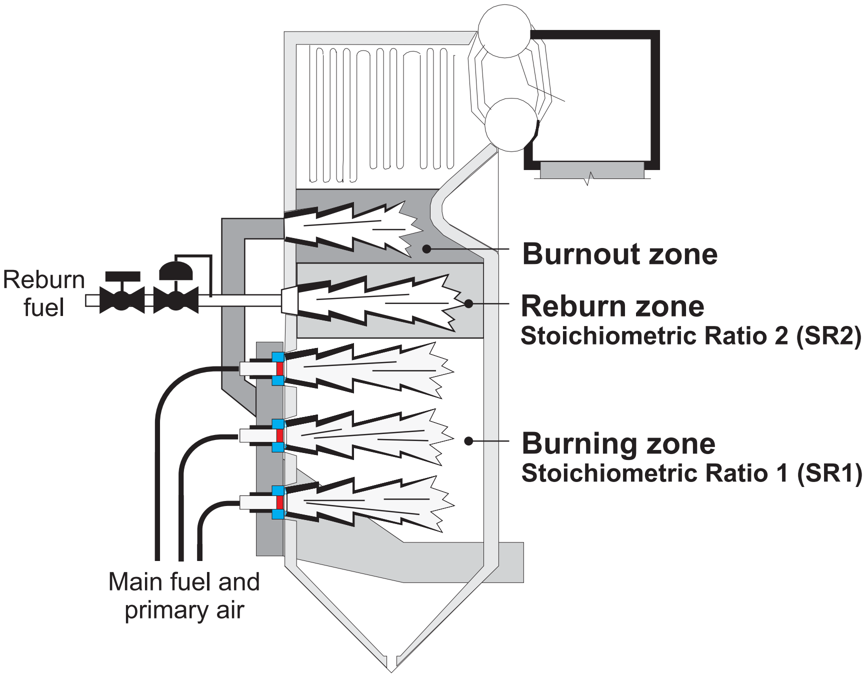


Figure 8-7. Boiler with stoichiometric ratios of 1 and 2

As shown in Figure 8-7, the burning zone operates air-rich with as low an excess air level as possible. Under these conditions, a stoichiometric ratio of 0.9 can be achieved in the reburn zone. A higher excess air in the primary combustion zone requires more reburn fuel to achieve this stoichometric ratio. Finally, in the burnout zone, excess air is added to achieve full oxidation of the combustion products.

> Application of reburning to cyclone boilers has demonstrated encouraging results. A recent test applied coal as the reburn fuel on a 110-MW electric utility facility.[1] A 110-MW unit was chosen partly because it provides a typical representation of cyclone boilers. NO_X emission reductions of 52% were experienced with bituminous coal at full load. Reburn allowed for process flexibility with only a reduction of less than 1.5% in boiler efficiency.

8.5 APPLICABILITY

8.5.1 Installation

Reburning can be applied to essentially any type of boiler, provided the gas stream residence time is long enough to allow the reburn fuel to burn completely.

Reburning can be performed by use of existing burner ports or by the installation of additional ports. Installations of additional ports specific for reburning typically produces lower NO_X emissions than use of existing ports.

Reburn technology can be applied to essentially all types of boilers provided that there exists sufficient distance above the elevation of the main coal burners to install the gas burners and the overfire air ports.[7]

An adequate distance between the primary burn zone and the reburn zone is required to provide the necessary residence time for burnout to occur. A residence time of at least 0.3 seconds is required to maximize the effectiveness of the reburn system.

8.5.2 Benefits

NO_X reductions associated with reburning can range from 40% to 70%, with an average reduction in the 50% to 60% range. Slight reduction of sulfur dioxide (SO_2), carbon dioxide (CO_2), particulate matter, and air toxics is accomplished by the reburn system. Reduction efficiencies of these pollutants are lower than NO_X reduction. The reductions are a result of reducing the primary fuel and using a cleaner fuel in the reburn zone. SO_2 reduction is directly proportional to the amount of natural gas substituted for primary fuel.

Reburning is advantageous because the system can be retrofitted to most types of existing boilers. Relative to other control technologies, installation costs are considered to be low or moderate and vary depending on the design of the boiler.

The capital cost for a coal-fired electric generating unit is approximately $30/KW,[8] although both capital and operating costs are site-specific.

Reburning is also attractive because it can be used in conjunction with other control techniques for further reduction of NO_X emissions.

8.5.3 Design

There are two general conditions for designing a reburn system. First, the reburn fuel must be injected at a location where the combustion temperatures are in the range of $1600^{o}F$ to $2200^{o}F$. Second, the residence time for reburn reactions in the gas phase must be at least 0.3 seconds.

The design approach varies with each boiler; however, in general, the reburn system can be designed either with or without a supplemental carrier gas stream. A supplemental carrier gas stream, such as flue gas recirculation, is typically associated with larger boilers.

Figure 8-8 illustrates the effect of reburn zone stoichiometry on NO_X emissions. The graph shows that NO_X emissions decrease as the stoichometric ratio decreases. The graph also shows that this relationship is true at various load levels. As previously stated, a stoichometric ratio of 0.9 is the target design value.

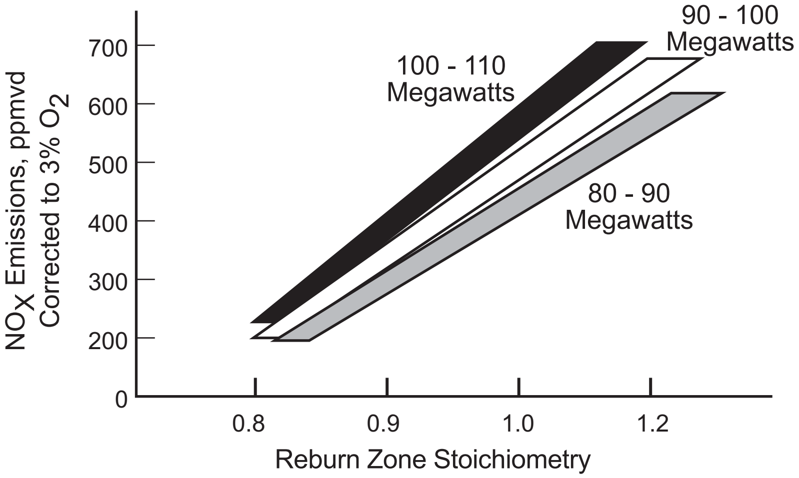


Figure 8-8. Effect of reburn zone stoichiometry on NO_X emissions

Figure 8-9 demonstrates the relationship of NO_X levels to reburn zone stoichiometric ratio, with no reburn and with reburn at various levels of fuel (i.e., natural gas) use. This data shows that NO_X emissions are reduced with the use of reburn. Furthermore, it shows that NO_X emissions are decreased as the usage of reburn fuel used increases.

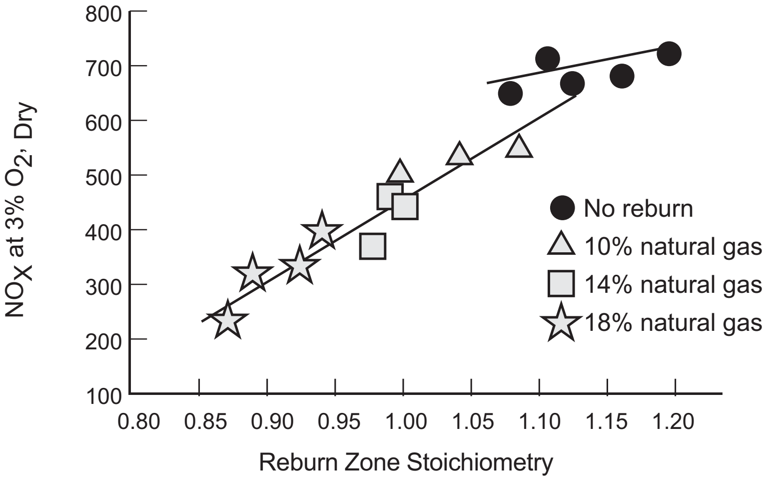


Figure 8-9. Relationship of NO_X levels to reburn zone stoichiometry

This figure demonstrates that the NO_X emissions progressively decrease from baseline levels as the reburn zone stoichiometry is reduced. The target stoichiometric ratio of 0.9 is achieved by using 18% of the fuel consumed as reburn fuel.

8.5.4 Limitations

Installation of new reburn burners and burnout ports requires penetration into the boiler wall, therefore requiring that the boiler removed from service. The tubes lining the boiler walls must often be modified in order to accommodate the new burners.

Higher fuel cost is a disadvantage of reburning. This is especially the case if the reburn fuel is expensive. Natural gas is often more expensive than the primary fuel. Coal used for reburn fuel may require additional pretreatment (e.g., pulverizing), thereby increasing operating costs.

Long-term data for reburning systems are not available due to the recent (mid-1990s) commercial application to large-scale units.

Boiler tube wastage occurs when there is poor heat exchange from the boiler tubes because of slagging or fouling. Tests have shown that conditions conducive to slagging and fouling can exist if too much air is injected into the reburn zone. This was especially true when the boiler was operated at low load and the reburn system was removed from service. Injecting a small amount of air through the burners to keep them cool prevents these conditions. Initial data suggest that boiler tube wastage is not typically a problem with NO_X reburn systems. However, boiler slagging, fouling, and boiler tube wastage require further study.

> *Slagging* is the formation of slag on boiler walls and tubes. *Fouling* is the buildup of fly ash on the boiler walls and tubes.

As shown in Figure 8-10, NO_X emission reductions obtained from the use of NO_X reburning are dramatically reduced at loads below 75 MW. As such, the use of reburning at low loads is not practical. However, NO_X reductions associated with the use reburning at moderate and high load levels are significant.

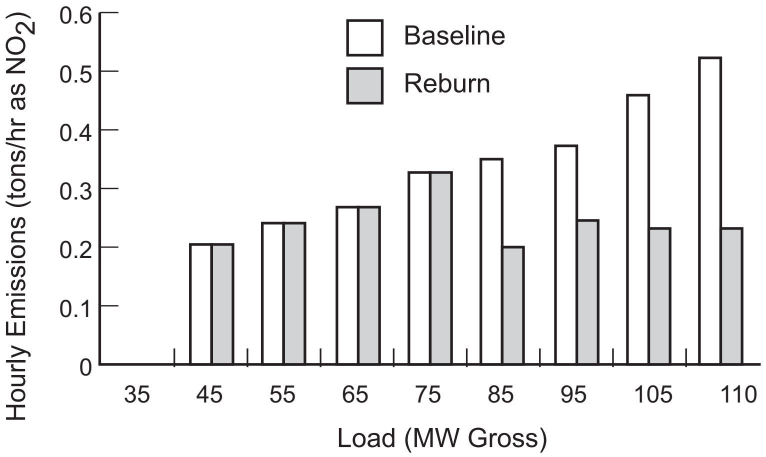


Figure 8-10. Impact of NO_X reburn at various loads

8.5.5 Reburning with Other Control Techniques

Due to the recent regulations concerning NO_X control, reburning may not be a sufficient stand-alone control technique. However, reburn can be applied in conjunction with other NO_X, SO_2, and particulate matter emission control techniques.

Reburn is often applied with flue gas recirculation, LNB, SCR (described in Chapter 11) and/or SNCR (described in Chapter 12) for additional NO_X reduction. Figure 8-11 displays the relative reductions established with no control, with low NO_X burners, and with reburning and low NO_X burners.

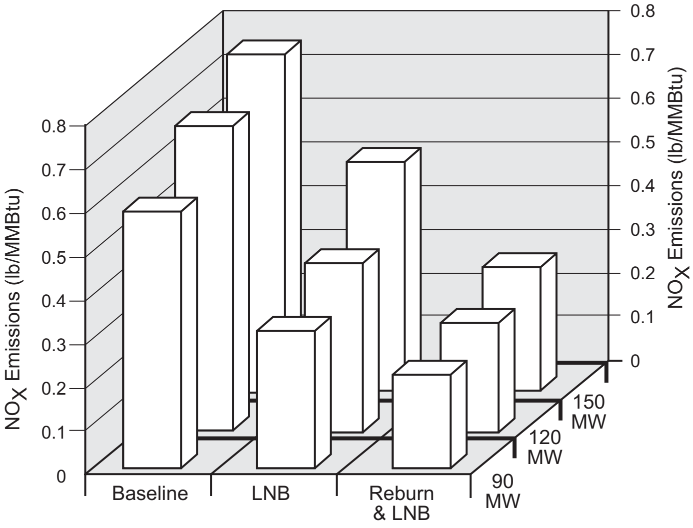


Figure 8-11. Emissions reductions associated with NO_X control technologies

---

This chart illustrates the combined effects of reburning and low NO_X burners (LNB). The baseline conditions (without reburning or LNB) are shown on the left. The baseline NO_X levels increase as the boiler load increases. This same load-related pattern of emissions is present after the application of LNB (center). LNBs decrease NO_X emissions to the 0.25 lb to 0.5 lb/NO_X per MMBtu. The addition of gas reburning with LNB is shown on the right. With the combined NO_X control, emissions are reduced to the 0.2 to 0.3 lbs. NO_X per MMBtu.

Review Exercises

1. What are typical control efficiencies for reburning?
   a. 15% to 20 %
   b. 30% to 40 %
   c. 50% to 70 %
   d. 80% to 95 %
   e. None of the above

2. The reburn zone is operated ______.
   a. sub-stoichiometric
   b. at stoichiometric conditions
   c. super-stoichiometric
   d. Operation is site-specific.
   e. None of the above

3. Reburning is ______.
   (Select all that apply.)
   a. off-stoichiometric combustion
   b. staged fuel combustion
   c. FGR
   d. BOOS
   e. None of the above

4. What species are formed in the reburn zone and are necessary for NO_X reduction?
   (Select all that apply.)
   a. CO
   b. HCN
   c. hydrocarbon radicals
   d. SO_2
   e. None of the above

5. Why is natural gas a preferable reburn fuel?
   (Select all that apply.)
   a. It is a relatively inexpensive fuel.
   b. It results in a reduction of SO_2 emissions.
   c. It is the only fuel that produces the required intermediate radicals for the reburning process.
   d. It provides rapid burnout.
   e. None of the above

6. What is an ideal stoichiometric ratio for operation of the primary zone?
    a. 0.8
    b. 0.9
    c. 1.0
    d. 1.1
    e. None of the above

7. What is fouling?
    a. Formation of slag on the walls and tubes of the boiler.
    b. Corrosion of the boiler tubes resulting from impurities in the fuel.
    c. Corrosion of the boiler tubes resulting from impurities in the feed water.
    d. Formation of fly ash on the walls and the tubes of the boiler.
    e. None of the above

8. Reburning typically reduces which of the following pollutants?
   (Select all that apply.)
    a. Particulate matter
    b. Nitrogen dioxide
    c. Sulfur dioxide
    d. Carbon dioxide
    e. None of the above

9. Reburn technology is currently applied to which of the following sources?
   (Select all that apply.)
    a. Electric generating units
    b. Municipal waste incinerators
    c. Asphalt concrete facilities
    d. Kraft pulp mills
    e. None of the above

10. The minimum residence time from the primary zone to the reburn zone should be
    ___________.
    a. 0.003 seconds
    b. 0.03 seconds
    c. 0.3 seconds
    d. 3.0 seconds
    e. None of the above

References

---

[1] Clean Coal Technology. May 1999. *Reburning Technologies for the Control of Nitrogen Oxides Emissions from Coal-Fired Boilers*. Topical Report Number 14.

[2] Pratapas, J. and J. Bluestein. May 1994. *Natural Gas Reburn: Cost Effective NO_X Control.* Gas-Based NO_X Control Information Center. Pages 47-50. Power Engineering.

[3] Englehardt, D. November/December 1999. *Update Reburn Experience.* Page 76. Power.

[4] Alexander’s Gas and Oil Connections. December 22, 1997. *Orimulsion Claimed to be Clean.* Company News-North America. Volume 3, Issue 28.

[5] Makansi, J. May 1993. *Special Report, Reducing NO_X Emissions from Today's Powerplants*. Pages 11-32. Power.

[6] Energy and Environmental Research Corporation. *Reburn: Cost Effective, Efficient NO_X Control.* Page 150.

[7] Gas Research Institute. Undated. *Natural Gas Reburning, Cost Effective Reduction for Utility Boilers.*

[8] Clean Coal Technology. September 1993. *Reduction of NO_X and SO_2 using Gas Reburning, Sorbent Injection and Integrated Technologies*. Topical Report Number 3.

9 Reciprocating Internal Combustion Engines

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you will be able to do the following:

1. Describe the dynamics of the fuel-to-air ratio.
2. State the differences between spark ignition and compression ignition engines.
3. Describe how each type of engine (spark ignition and combustion ignition) contributes to NO_X emissions.
4. Identify the pre-combustion and post-combustion emission reduction control options.
5. Explain how the different types of catalysts work to reduce emissions.

9 Reciprocating Internal Combustion Engines

Note: The broadcast video segment associated with this chapter addresses a case study in the control of NO_X emissions from Navy diesel engines (see section 9.3).

Individually, a small reciprocating internal combustion (IC) engine, such as an automotive engine, contributes an insignificant amount of NO_X to the atmosphere. However, as shown in Chapter 3, automotive engines as a group emit the majority of total anthropogenic NO_X. Controlling these small sources is a challenging problem because of (1) the variety of individual designs, (2) the large load swing demands of the engines, and (3) the numerous sources to be serviced and inspected. Far fewer large IC reciprocating engines (e.g., Navy diesel ship engines) exist, but their combustion controls and regulations have lagged behind small IC engines.

The major emissions of IC engines are NO_X, CO, hydrocarbons (HCs), and particulate matter. The relationship of these pollutants, engine efficiency, and engine performance must be understood in order to retrofit the best control options.

9.1 PRE-COMBUSTION CONTROL

9.1.1 Spark Ignition Engine Combustion

Figure 9-1 displays the relative concentrations of NO, unburned hydrocarbons, and carbon monoxide emitted under air-fuel equivalence ratios for a typical spark ignition (SI) IC engine burning a hydrocarbon (HC) fuel. The equivalence ratio is defined in Equation 9-1. For an equivalence ratio less than 1.0 the engine is operating under lean conditions because excess air is added. An equivalence ratio greater than 1.0 indicates that the engine operates fuel-rich and that excess fuel is being used. Spark ignition IC engines typically operate at an equivalence ratio of 0.7 to 1.4 to obtain good combustion in a short residence time.

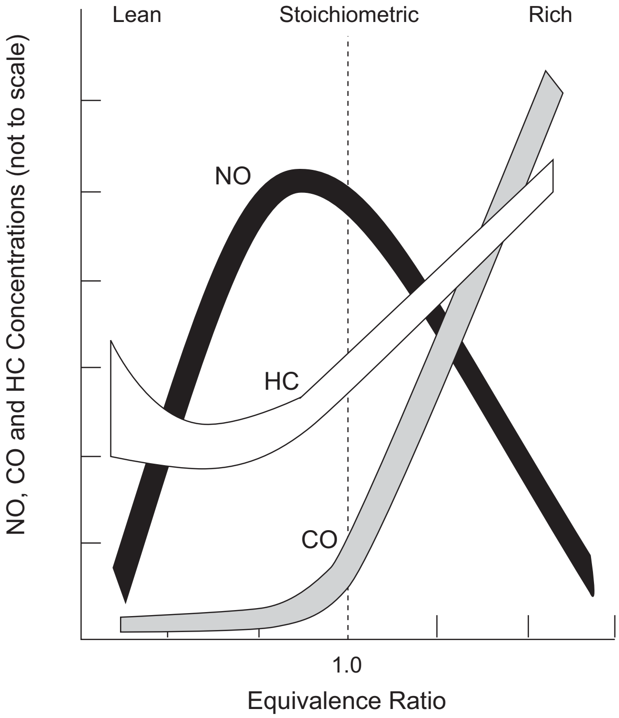


Figure 9-1. Emissions relative to air-fuel equivalence ratios (ϕ) for a typical spark ignition IC engine [1]

$$\phi = \frac{\textit{stoichiometric air - fuel ratio}}{\textit{actual air - fuel ratio}} \qquad \text{Equation 9-1}$$

As seen in Figure 9-1, NO formation is greatest for slightly lean conditions (i.e., ϕ=0.95). The maximum combustion temperature occurs at ϕ=1.0 creating favorable conditions for NO_X formation. The NO_X formation rate increases as a minor amount of excess oxygen is provided. As more excess air is added the combustion temperature decreases and NO_X emissions are reduced. Engines run fuel-rich during periods of increased demand of power (i.e., acceleration), and the more fuel-rich the engine runs, the greater the emissions of unburned hydrocarbons and carbon monoxide.

The emissions of CO and unburned hydrocarbons are also greatest when the engine is cold (e.g., start-up). However, NO_X formation occurs when combustion temperature, pressure, and residence time are highest. This is because most of the NO_X formation for spark ignition IC engines can be attributed to thermal NO_X. Fuel NO_X contribution is low because most commonly used fuels, such as gasoline and diesel, have inherently low levels of organically-bound nitrogen. Only engines that burn residual or crude oils will form significant portions of fuel NO_X.

The flame front originates at the spark plug where combustion in the cylinder is initiated. The slug of gas in the cylinder closest to the spark plug reaches the greatest temperature and pressure. This slug of gas has the greatest residence time at an elevated temperature and pressure, often allowing NO_X formation to reach equilibrium. The slugs of gas farthest from the spark have lower temperatures, pressures, and residence times, and NO_X formation generally does not reach equilibrium in these areas.

Following combustion, the cylinder cools quickly, not allowing NO_X to reach equilibrium at the lower temperatures, and the NO levels become "frozen". Since the pressures in a spark ignition IC engine are much higher than ambient pressure (typically 10 to 15 atm for gasoline engines), NO_X equilibrium levels in the cylinder are high. NO_X emissions will, on average, exceed the exhaust gas equilibrium levels.

Reduction of NO_X formation is achieved by reducing the peak combustion temperature, pressure, and residence time, or by creating a homogeneous gas-to-air distribution. The following parameters represent some of the most important design and operating variables affecting the formation and emissions of NO_X.

- Air-fuel equivalence ratio
- Cylinder gas compression ratio
- Spark timing
- Combustion chamber design
- Exhaust gas recirculation (EGR)

Combustion-based NO_X control techniques occur at the expense of power, performance, and an increase of other pollutants. The control of NO_X must be made while recognizing and balancing these other variables.

9.1.1.1 Air-to-Fuel Equivalence Ratio

The air-fuel ratio is important in controlling not only NO_X emissions, but also carbon monoxide and unburned hydrocarbons. When adjusting the air-to-fuel ratio NO_X emissions should be balanced against CO emissions, hydrocarbon emissions and engine efficiency.

NO_X emissions are reduced under fuel-rich operating conditions because of limited oxygen and peak temperatures. However, the emissions of both CO and HCs are likely to increase because of incomplete combustion.

Modern automobiles control the air-to-fuel ratios with "on-board" computers. The computer regulates the fuel based on oxygen measurements taken from the combustion products exiting the engine. Oxygen is maintained at a level to give the optimum performance of the catalyst. (Catalysts for spark ignition IC engines are discussed later in this chapter.) However, during periods of "hard" acceleration the fuel is not regulated and emissions control is sacrificed for increased engine performance.

9.1.1.2 Cylinder Gas Compression Ratio

The compression ratio is defined in Equation 9-2. Top dead center (TDC) is the volume in the cylinder when the piston is at the upper limit while bottom dead center (BDC) is the cylinder volume when the piston is at the lower limit (see Figure 9-2).

$$r_v = \frac{\text{volume at BDC}}{\text{volume at TDC}} \qquad \text{Equation 9-2}$$

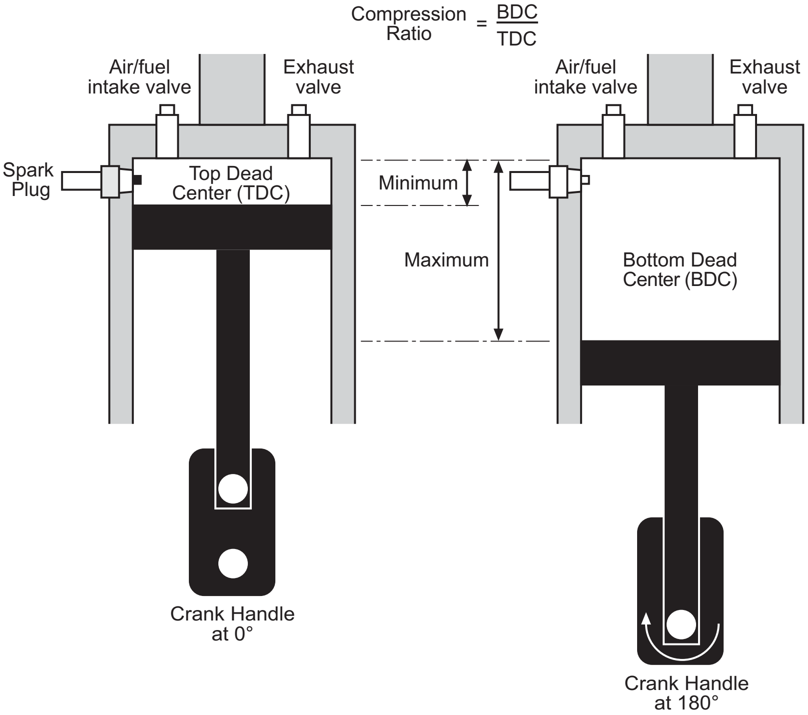


Figure 9-2. TDC and BDC piston positions

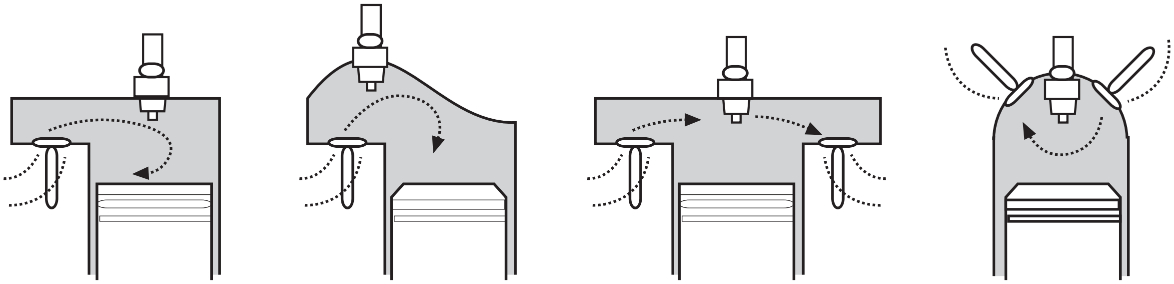
NO_X formation can be limited by reducing the compression ratios, thereby lowering peak temperatures within the cylinder. However, lower compression ratios also reduce the engine efficiency and are not the preferred control technique for gasoline engines.

9.1.1.3 Spark Timing

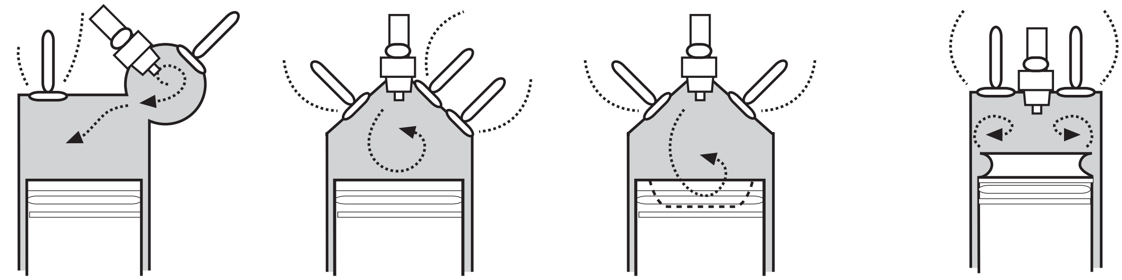
Proper spark timing adjustment can reduce NO_X emissions. The best engine performance is obtained by timing the spark about 20° prior to TDC. Retarding the ignition will reduce residence time, lower peak temperature and delay peak pressure during the engine cycle. For comparable reductions in NO_X emissions, engine performance is affected less by spark timing retardation than by reduced compression ratios. A NO_X reduction of 50% can be obtained by firing the spark at TDC for mobile spark ignition IC engines.[1]

9.1.1.4 Combustion Chamber Design

Several chamber designs for a mobile spark ignition IC engine are shown in Figure 9-3. Flame speed and residence time are altered by the design of the combustion chamber. For example, the wedge chamber is designed to control detonation, the hemispherical chamber is designed to provide greater power, and the stratified charge chamber is designed to lower emissions. The stratified design pre-ignites a fuel-rich mixture in a separate chamber. The flame front then enters the main combustion chamber, which contains a lean fuel mixture. Pre-igniting the air-fuel mixture in the absent of excess oxygen limits NO_X formation.



Nonturbulent L Turbulent (wedge) L Nonturbulent T Hemispherical



Honda stratified charge MCA jet valve Scooped bowl piston Sonic pulse burn

Figure 9-3. Spark ignition combustion chamber designs [1]

9.1.1.5 Exhaust Gas Recirculation

EGR can reduce NO_X emissions by 10% to 20%. (See Equation 9-3.) EGR systems recirculate as much as 15% to 20% of the combustion gas products and excess air. The mixture enters the cylinders and dilutes and cools the combusting gases. The penalty for EGR includes the possibility of slight reduction of engine efficiency, significant loss of power, engine misfiring and increased carbon monoxide and hydrocarbon emissions.

$$EGR = \left(\frac{\dot{m}_{EGR}}{\dot{m}_i}\right)100 \qquad \text{Equation 9-3}$$

Where:

$\dot{m}_{EGR}$ = total mass flow recycled
$\dot{m}_i$ = total mass flow into cylinders

9.1.1.6 Other Variables

Vehicle emissions are directly related to driving habits and driving conditions. Emissions increase dramatically during “hard” acceleration (NO_X, CO and HCs) and “cold” starts (CO). The average speed, driving terrain, and frequency of starts and stops also impact vehicle emissions. The variation in emissions for different load conditions of an SI mobile engine is shown in Table 9-1. Emissions for stationary spark ignition IC engines also vary dramatically with load requirements.

Table 9-1
Typical Spark Initiated Uncontrolled Emissions[2]

Pollutant	Units	Idling	Acceleration	Cruise	Deceleration
NO_X (as NO_2)	ppm	30	1,200	650	30
	lb/hr	0.0015	0.92	0.12	0.0015
HC (as CH_3)	ppm	10,000	6,000	5,000	30,000
	lb/hr	0.15	1.42	0.28	0.46
CO	percent	5	5	0.6	5
CO_2	percent	9.5	10	12.5	9.5

Modern automotive engines with proper maintenance contribute fewer emissions per mile than older or poorly maintained vehicles. Maintenance for emission reduction includes cleaning spark plugs, timing adjustment, and oil changes.

9.1.2 Compression Ignition Engine Combustion

Compression ignition (CI) engines, such as diesel engines, operate at higher pressures than gasoline engines. The auto-ignition point of diesel fuel in the cylinder is approximately 1300°F at 44 atm. Higher pressure results in greater NO_X formation and lower CO formation. The equilibrium equation for the global reaction of NO formation (Reaction 2-1) is shown in Equation 9-4.

$$K_p(T) = \frac{y_{NO}P}{\left(y_{O_2}P\right)^{1/2}\left(y_{N_2}P\right)^{1/2}} = \frac{y_{NO}}{\left(y_{O_2}\right)^{1/2}\left(y_{N_2}\right)^{1/2}} \qquad \text{Equation 9-4}$$

Equation 9-4 shows that NO equilibrium is temperature-dependent. Although the pressure terms cancel out in the equilibrium equation, pressure is still directly related to NO_X formation through inter-molecular kinetics. Increased inter-molecular kinetics result in more molecular collisions, thereby increasing the rate of NO_X formation.

Spark ignition engines (e.g., gasoline-fueled) run fuel-rich, while diesel engines operate on a fuel-lean basis. NO_X emissions are higher for CI engines than for SI engines because of the excess air and high compression ratios. Compression ratios are approximately 11.5:1 to 22:1 for CI engines and about 9:1 to 12:1 for SI engines.

Control measures used for CI engines are similar to those for SI engines. These include combustion chamber design, compression ratio reduction, fuel-air equivalence adjustment, and EGR. In addition, engine combustion control techniques for CI engines include injection retardation, pre-chamber combustion designs, inlet air temperature reduction, and water injection. Table 9-2 displays the fuel consumption necessary to maintain a rated power output, which serves as a direct indication of engine efficiency change. The associated changes in NO_X emissions are also shown.

Table 9-2
Compression Ignition NO_x Control Methods[3]

NO_X Control Technique	Fuel Consumption (Change)	NO_X Emissions (Reduction)
Prechamber Designs	8% to 15%	50%
Indirect Injection	3%	40% to 50%
Exhaust Gas Recirculation	4%	45% to 55%
Injection Retardation	2% to 5%	15% to 35%
Water Injection	-2% to 0%	35%
Inlet Air Temperature Reduction	-2%	12%

9.1.2.1 Pre-Chamber Designs/Indirect Injection

Pre-chamber designs, indirect injection, improved nozzle design, and higher injection rates are often used in combination for controlling emissions. These design features increase the mixing of air and fuel by increasing turbulence and producing finer fuel droplets. Improved nozzle designs and increased injection pressure produce finer fuel droplets that vaporize quickly. Similarly, hot surfaces are also used to evaporate injected fuel, making it highly combustible.

Pre-chamber design, termed *clean burn* technology, is a popular NO_X control technique. By pre-mixing the air and fuel in a pre-chamber (indirect injection) the fuel is completely vaporized prior to entering the main combustion chamber through an orifice. Although the homogeneous air-fuel mixture results in lower emissions, the pressure drop created by the orifice reduces the engine efficiency. Pre-combustion chambers are used primarily for high velocity (2,000 to 4,000 RPM) diesel engines (i.e., small mobile sources).

Large stationary IC engines operate at much lower engine speeds (i.e., 110 to 400 rpm). Indirect injection and pre-chamber designs are generally not necessary for larger IC engines, because greater time is available for air-fuel mixing.

9.1.2.2 Injection Timing Retardation

Injection timing retardation (TR) for CI engines is a control technique based on the same principle as spark retardation of SI engines. NO_X formation is reduced by delaying the timing of fuel injection in the engine cycle. Delaying the ignition of fuel also lowers the residence time of combustion gases at elevated temperatures and pressures. Injection timing is a common control technique for both on-road and off-road vehicles. This is an inexpensive control technique that is used in conjunction with other control options. CO and particulate matter emissions must also be balanced with the reduction of NO_X by adjusting the injection timing and the EGR ratio.

9.1.2.3 Water Injection/Emulsified Fuel

Water injection/emulsified fuel techniques can be effective for reciprocating engines. Adding a heat sink in the form of water reduces combustion temperature. However, the enthalpy required to heat the water reduces engine efficiency.

Moderate to large stationary engines can greatly benefit from water injection. However, the inaccessibility of clean water has somewhat limited the application to smaller or mobile reciprocating engines. Because salts and minerals in non-potable water can severely damage engine components, emulsified fuel is a more practical option for many of these sources. Emulsified fuel is obtained by pre-mixing suitable water with the fuel in a specific ratio. This approach limits NO_X emissions without the use of a separate water injection system. Although CO is not substantially affected by the addition of water, increased hydrocarbon emissions are possible.

9.1.2.4 Inlet Air Temperature Reduction

Inlet air temperature reduction is a control technique for larger off-road engines, where the temperature of inlet air is reduced to lower the peak combustion flame temperature.

9.2 POST-COMBUSTION CONTROL

Add-on pollution control technology has been applied to vehicles for the past twenty-five years. The dominant post-combustion control for IC engines is the catalytic converter, which is mounted in the exhaust gas flow system. The catalyst is contained on a porous ceramic honeycomb or ceramic granular medium. Catalytic converters installed on CI engines require greater gas flow than SI engines because of the higher levels of particulate matter in the gas stream.

9.2.1 Spark Ignition Engines

9.2.1.1 Oxidation Catalyst

The original catalyst installed on mobile vehicles was a simple oxidation catalyst, which accelerates the oxidation of CO and HCs. CO is oxidized to CO_2, while hydrocarbons are oxidized to CO_2 and H_2O. NO_X emissions are not affected by this catalyst design.

9.2.1.2 Dual-Bed Catalyst

The next major catalyst design, the dual-bed catalyst, places an additional bed (Bed 1) upstream of the oxidation catalyst (Bed 2). Emissions exiting the combustion cylinders enter Bed 1, where NO emissions are reduced to molecular nitrogen. In order for Bed 1 to operate efficiently, the oxygen level in the entering gas stream must be limited. To reduce the oxygen level, the engine must operate fuel-rich, which decreases fuel efficiency. In Bed 2, the oxidation catalyst requires excess oxygen to function properly. To increase the oxygen level, excess air is added to the gas stream before it enters Bed 2.

The dual-bed catalyst proved to be unpopular because of the fuel loss associated with it. To overcome this disadvantage, the three-way catalyst design was developed.

9.2.1.3 Three-Way Catalyst

The three-way catalyst is an efficient post-combustion control for use under controlled conditions in modern passenger cars, light duty trucks, and heavy-duty trucks. Emissions reduction is accomplished with a rhodium catalyst (for NO) and a platinum or palladium catalyst (for CO and hydrocarbons). The three-way catalyst is very effective in a narrow equivalence ratio window, as shown in Figure 9-4.

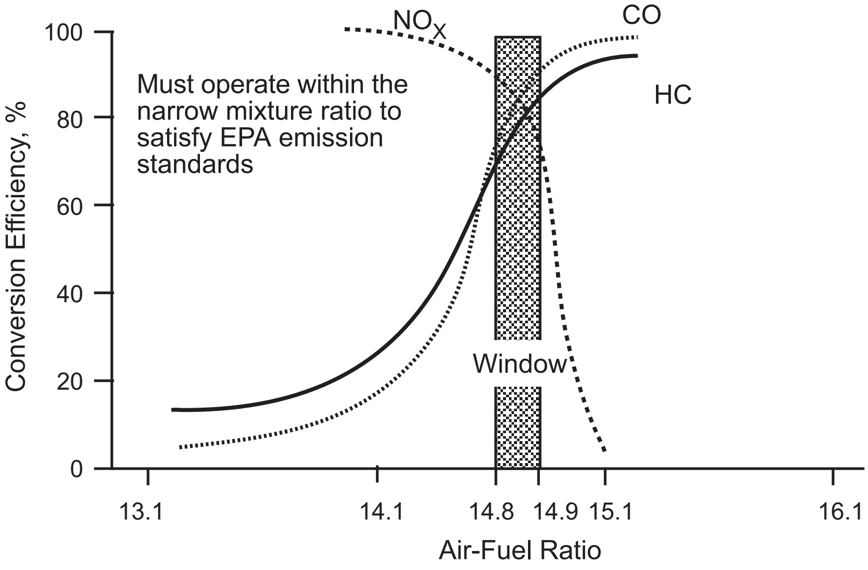


Figure 9-4. Operating window for efficient operation of a three-way catalyst[4]

During operation, a computer monitors a "real-time" oxygen sensor located at the inlet to the catalyst and controls the air-to-fuel ratio to provide optimal catalyst performance. Restriction of the air-fuel mixture limits engine performance, therefore, during periods of increased power demand (quick acceleration), the computer does not limit fuel use and the catalyst becomes inefficient in controlling CO and hydrocarbon emissions.

The three-way catalyst operates in a specified temperature window and is not effective unless heated sufficiently by exhaust gases. During the first few minutes after start-up of a cold engine, emissions are not controlled. The relationship between catalytic converter temperature and emission control efficiency is shown in Figure 9-5. The *light-off point* is the temperature at which the catalyst reaches 50% efficiency.

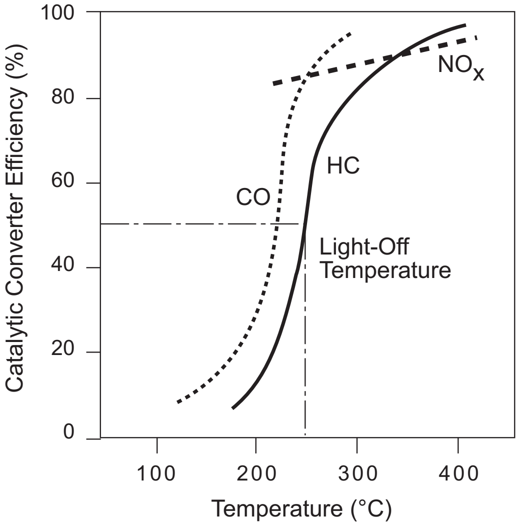


Figure 9-5. Relationship between emissions control efficiency and temperature of a typical catalytic converter

If the catalyst becomes hot, SO_2 can be reduced to H_2S, which has an obnoxious "rotten egg" odor. Excessive heat can also sinter the catalyst, destroying the activating pores rendering the catalyst useless. Thermal degradation occurs at temperatures greater than 900°F.[5]

Catalysts are also vulnerable to a number of impurities. The catalyst material can be poisoned by fuel impurities such as lead and sulfur. Gasoline containing even a small amount of lead will destroy the catalyst. Components in lubricating oil such as zinc, phosphorus, antimony, calcium, and magnesium are also poisonous to the catalyst.

9.2.2 Compression Ignition Engines

Post-combustion techniques tend to be more expensive and complex than pre-combustion techniques. Chemical additive and water injection systems are generally applicable to large stationary CI sources. Trap-oxidizers, catalysts and emulsified fuels can be used with a greater variety of CI sources.

9.2.2.1 Catalysts

Catalyst designs such as those discussed for SI engines have limited effectiveness in reducing NO_X emissions, because compression engines tend to operate fuel-lean. The relationship of typical catalytic converter emissions control efficiency to the equivalence ratio is shown in Figure 9-6.

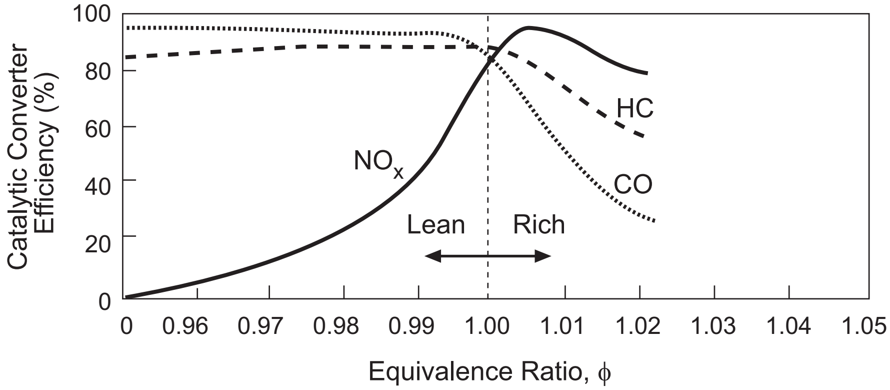


Figure 9-6. Relationship of typical catalytic converter emissions control efficiency to the equivalence ratio

Catalysts designed to control NO_X under fuel-lean conditions are available. A catalyst consisting of platinum and rhodium with alkaline rare earths is applied to lean-burning engines.

9.2.2.2 Trap-Oxidizer

The trap-oxidizer is a post-combustion device currently applied to various diesel engines. The trap-oxidizer consists of a catalytic converter and a particulate matter filter. The traps remove 60% to 90% of the particulate matter.[3] Particulate matter must be removed or ignited to prevent backpressure in the combustion chambers. Backpressure increases combustion temperature, giving rise to NO_X formation.

9.2.2.3 Chemical Flue Gas Additives

Cyanuric acid has had limited application to large stationary CI engines. Solid cyanuric acid sublimes to form isocyanides, which react with flue gas to reduce NO_X to N_2, CO_2, and water vapor. NO_X emissions produced by large CI engines may also be controlled by ammonia injection systems. The problem with chemical additive systems is that they are expensive and require hazardous chemical tanks located near the source, an undesirable arrangement, even on large mobile sources such as ships.

9.2.2.4 Water Injection/Emulsified Fuel

Water injection and emulsified fuel techniques are applied in a manner similar to SI engine applications. However, water injection has not proven useful for most large mobile CI sources because of inaccessibility of sufficient clean water. For example, although large Navy diesel engines are an ideal application for emulsified fuel, it is not practical for Navy ships to carry the required amount of clean water or a device for removing impurities of sea water for injection.

Control of stationary reciprocating off-road IC engines has lagged behind on-road sources, partly because of the more stringent regulatory requirements for mobile sources and the limited control options available. Large CI sources such as ship engines were not regulated until fairly recently. Off-road sources are currently a proportionally greater contributor to non-attainment of air quality goals.

9.3 CASE STUDY

This case study on the control of diesel engines is based on the results of a joint project between the U.S. Navy and EPA. The Navy operates many diesel engines on its land-based facilities and ships and is interested in controlling emissions from these engines so that they meet all applicable emissions standards. The Strategic Environmental Research and Development Program (SERDP) and EPA funded the project jointly.

SERDP is the Department of Defense (DoD) corporate environmental research and development (R&D) program, planned and executed in full partnership with the Department of Energy (DOE) and EPA, with participation by numerous other federal and non-federal organizations.

The objective of this diesel engine research project was to develop a cost-effective approach to controlling NO_X and PM emissions from the Navy's shipboard diesel engines to meet future applicable emissions standards. Because the Navy operates its engines under a variety of conditions, it was necessary to address factors that are not normally considered when examining controls for stationary engines.

An examination of the population of diesel engines operated by the Navy reveals that these engines fall into two primary categories. The first category is generators that are used for both long-term use and emergency use. The second category is propulsion engines that are used on board ships. These propulsion engines operate under variable loads as the speed of the ship changes.

As shown in Table 9-3, EPA proposed NO_X, HC, CO, and PM emission standards for marine diesel engines in 1994. Control technologies examined in a laboratory setting have been demonstrated to achieve the necessary NO_X reductions but they also resulted in an increase in HC, CO and PM emissions.

Table 9-3
Proposed U.S. EPA Marine Diesel Emission Standards

Pollutant	Limit, g/kW-h
NO_X	9.2
HC	1.3
CO	11.4
PM	0.54

Source: 40 CFR 91, Federal Register 55930, November 1994

Most of the Navy’s diesel engines (63%) are two-stroke engines. Consequently, a four-cyclinder, two-stroke DDC series 71 model engine with a power output of 135kW was selected for this research project. This model was also selected because it was compatible with the capabilities and limitations of the research facility. As shown in Figure 9-7, the manufacturer’s data for this model indicates that the proposed NO_X limit is exceeded when the unit operates above a 50% load.

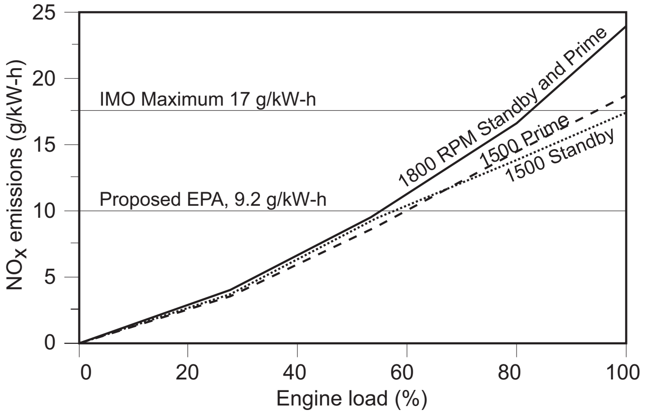


Figure 9-7. NO_X emissions at specific engine loads

9.3.1 Test Design

The test engine was mounted in the test facility and hooked up to a load bank. A *load bank* is an electrical device that applies electrical load to a generator. The research facility is equipped with fuel storage tanks of capacities that provide constant fuel flow to the test engine. The test engine was equipped with data acquisition equipment, including continuous emissions monitors for CO, NO_X, HCs, O_2, and CO_2. All of the collected data was fed into the computer based data acquisition system.

PM sampling was not automated; rather a PM sampling train was operated to collect PM data on a periodic basis. A muffler/thermal oxidizer was added to the exhaust stream for noise control purposes. Finally, dioxin sampling was performed, but no dioxin was detected.

9.3.2 Candidate NO_X Control Technologies

Several NO_X control technologies were evaluated for inclusion in this research project. The first technology to be considered was injection *timing retardation*. Timing is the relationship of when fuel is injected into the cylinder relative to the position of the cylinder. The closer ignition occurs relative to the top dead center (TDC) of the piston, the better the efficiency. However, this causes problems from an operational standpoint and increases emissions of CO, HCs and PM. Nevertheless, this is the simplest and least expensive technique, and it can be applied to almost any type of engine. Consequently, this control technique was included in the test program.

Internal exhaust gas recirculation was also examined for inclusion in the test program. However, this technology is difficult to implement and was not tested on the subject test engine.

External exhaust gas recirculation returns gases from the engine exhaust to the engine as part of the air intake. This technology was included in the test program.

Water injection involves emulsifying the fuel with water and injecting the fuel-water mixture into the engine. This technique is very efficient in terms of NO_X reduction. However, the method requires that adequate supplies of potable water be available to emulsify the fuel, and a ship has limited access to potable water. Consequently, this control technique was not tested on the subject test engine.

Catalytic after-treatment is an effective NO_X control technique, but is very expensive because of the reagents that must continuously be added upstream of the catalyst. In addition, these reagents are very dangerous and their use on a ship creates serious safety issues. Consequently, this control technique was not tested on the subject test engine.

Electronic engine control applications are unique to individual engines. They require a significant effort to develop and have limited applicability to engines other than the one for which it was developed. For this reason, electronic engine controls were not tested on the subject test engine.

In summary, the two NO_X control technologies that were selected to be the main focus of this research project were injection timing retardation and external EGR.

9.3.3 Other Candidate Control Technologies

Because PM, CO and HC emissions increase with the use of NO_X control technologies, the test program examined the control of all these other pollutants. Candidate technologies included oxidation catalyst, particulate matter traps and fuel additives. Because data indicated that the oxidation catalyst (i.e., oxidizer) was adequate for control of all the non-NO_X pollutants, the oxidation catalyst was the only control technology used.

9.3.4 Summary of Test Results for Generators

Table 9-4 presents the test results from the research phase of this project. As demonstrated by the baseline levels, the test engine has high NO_X emissions and does not meet the proposed NO_X emission standard (9.2

g/kW-h). On the other hand, the PM and CO levels do comply with the proposed emission standards without any additional control.

Table 9-4
Navy Diesel Engine Test Results

Pollutant	Emissions (g/kW-h) at 100% load (135 kW)						
	Baseline	TR (6.9°)	EGR (10%) TR (6.9°)	EGR (10%) TR (6.9°) Oxidizer Intercooling	EGR (18%) TR (6.9°) Oxidizer Intercooling	Proposed U.S. EPA Standard	EGR (10%) TR (6.9°) Oxidizer
NO_X	26.61	16.82	12.65	10.2	9.0	9.2	11.73
CO	2.68	5.95	15.79	0.25	0.27	11.4	0.25
PM	0.096	0.24	0.61	--	0.25	0.54	0.25

Although timing retardation substantially reduces NO_X emissions, the engine still did not comply with the proposed NO_X standards. In addition, timing retardation increased the emissions of PM and CO. The next control level combined 10% EGR with timing retardation, resulting in reduced NO_X emissions but increased emissions of PM and CO. At this point, the emissions of NO_X still exceeded the proposed standard and now so did the emissions of PM and CO.

Application of an oxidizer with EGR and timing retardation reduced the CO and PM emissions such that the proposed standards were met. However, the NO_X emissions, although reduced, still did not comply with the proposed NO_X standard.

The addition of an intercooler between the supercharger and the intake reduced NO_X emissions, but still not enough to comply with the proposed NO_X standards. Only when the recirculated exhaust gas was increased to 18% in combination with all the other controls applied (i.e., timing retardation, oxidizer, intercooling) did the NO_X emissions comply with the proposed emission standard.

9.3.5 Summary of Test Results for Propulsion Engines

The research design for the propulsion engines was similar to that for the generator, except that the load bank was replaced with a dynamometer. The dynamometer was operated at variable speeds to simulate conditions associated with ship engines.

Table 9-5 shows the results of testing the engine at various speeds. At 1800 RPM (full load for a propulsion engine) and baseline conditions (no emission controls), NO_X emissions exceed the proposed NO_X emission standard. However, both the PM and CO standards were met. Applying 17% EGR, timing retardation, oxidizer, and intercooling result in a significant reduction in NO_X emissions. With these controls, the engine was able to comply with all proposed standards at a load of 1800 RPM.

Table 9-5
Navy Diesel Dynamometer Test Results

Pollutant	Engine Load								U.S. EPA Proposed Standard
	1800 RPM		1650 RPM		1500 RPM		1350 RPM		
	Emissions (g/kW-h)								
	Baseline ∗	Low NO_X ◊	Baseline ∗	Low NO_X ◊	Baseline ∗	Low NO_X ◊	Baseline ∗	Low NO_X ◊	
NO_X	22.95	8.99	21.70	8.16	22.50	9.44	18.76	8.81	9.2
CO	0.04	0	0.02	0.1	0.02	0	0.03	0	11.4
PM	≤0.1	0.166	--	0.295	--	0.385	--	0.597	0.54

∗ With no EGR, timing retardation, oxidizer and intercooling.
◊ With 7% EGR, timing retardation (6.9%), oxidizer, and intercooling.

At lower loads, NO_X emissions were significantly reduced when using all control methods. With the exception of the 1500 RPM test, the engine was able to meet the proposed NO_X standard; PM emissions increased with decreased load. At 1350 RPM the engine was unable to demonstrate compliance with the proposed standard for PM.

9.3.6 Field Testing

The purpose of field testing is to demonstrate that the system developed in the research phase of the project can work on a ship propelled by a diesel engine. The Navy selected a YP-676 Class yard patrol craft to be retrofitted with the laboratory engine modifications that proved successful in meeting the proposed emission standard.

The yard patrol boat uses a twelve-cylinder engine similar to the four-cylinder engine used in the laboratory tests. However, the yard class boat operates at a much higher load than the engine used in the laboratory tests. This required that the engine modifications be redesigned. These engine modifications included EGR, timing retardation (accomplished with new injectors) and oxidizer. Because the boat engine did not have a turbocharger, there was no need to include the intercooler as part of the engine modifications. Timing retardation was accomplished through the installation of a new injector provided by the engine manufacturer. Another limitation that existed on the boat, but not in the laboratory, was that the modifications had to made in a manner that did not interfere with operation of the boat.

Figure 9-8 compares NO_X emissions from the engine at baseline conditions and with the engine modifications. Using only the engine modifications *timing retardation* and *oxidizer*, NO_X was reduced to levels similar to those achieved in the laboratory tests. These levels are below the proposed NO_X emission standard. The NO_X levels associated with timing retardation, oxidizer and EGR are also shown. Although the use of EGR provides a further reduction in NO_X emissions, it is not necessary to meet the proposed NO_X emissions limits.

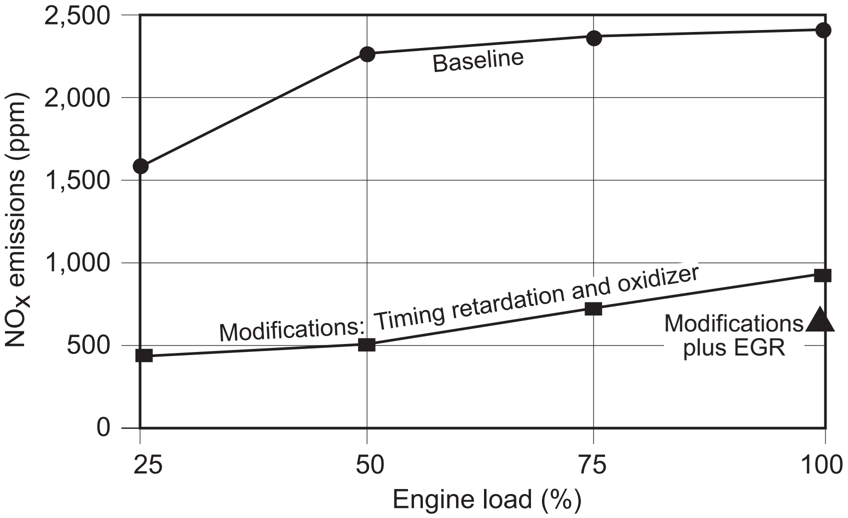


Figure 9-8. Effect of engine modifications on NO_X emissions

Figure 9-9 presents the results of the engine modifications on CO emissions. The use of timing retardation and oxidizer results in CO levels that are well below the baseline uncontrolled levels and meet the proposed CO emission limits.

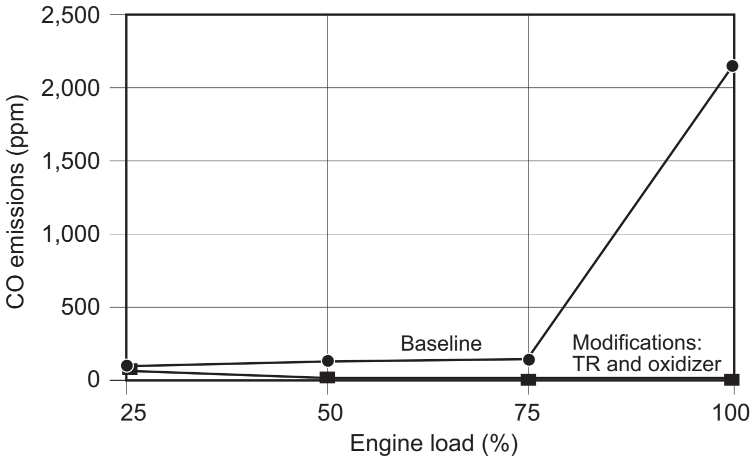


Figure 9-9. Effect of engine modifications on CO emissions

It was not possible to conduct PM testing during the field test because of space limitations on the boat. Also, because the hydrocarbon analyzer was not available during the duration of the field test, hydrocarbon testing was performed only on an intermittent basis. However, the testing that was conducted showed results similar to those obtained in the laboratory tests.

9.3.7 Conclusions

The program was successful in identifying engine modifications that can achieve the proposed emission standards for NO_X, CO and PM. Specifically, NO_X and CO emissions from a diesel test engine were reduced through a combination of timing retardation, external EGR, and use of an oxidizer. PM emissions remained unchanged.

Preliminary results from onboard ship tests showed similar reductions of NO_X and CO. The tests showed that the proposed emissions standards can be achieved through the use of cost-effective methods that do not disrupt onboard activities, do not reduce available fuel storage space, and do not require the storage of hazardous materials on board. However, it should be noted that this research project did not examine the long-term viability of these engine modifications to achieve compliance with the proposed emission limits on a long-term basis.

Review Exercises

1. Why do CI engines typically emit higher NO_X emissions than spark ignition engines?
   a. CI fuels (diesel) have higher N content than SI fuels (gasoline).
   b. CI engines cool more rapidly than SI engines.
   c. CI engines generally run at a lower speed than SI engines.
   d. CI engines operate at higher pressures than SI engines.
   e. All of the above

2. Diesel engines generally operate at which of the following conditions?
   a. $\phi < 1$
   b. $\phi > 1$
   c. $\phi = 1$
   d. None of the above

3. When the air-fuel ratio for an SI engine is increased beyond ideal stoichiometric conditions, which of the following is likely to occur?
   (Select all that apply.)
   a. NO_X emissions will increase
   b. CO emissions will increase
   c. Hydrocarbons will increase
   d. Catalytic control efficiency will increase
   e. None of the above

4. Why is NO_X formation in CI engines greater than in SI engines?
   (Select all that apply.)
   a. CI fuels contain less nitrogen
   b. CI engines run slightly fuel-lean
   c. CI engines operate at higher pressures
   d. CI engine speeds are higher
   e. None of the above

5. Damage to catalysts can occur from which of the following?
   (Select all that apply.)
   a. Lead in the fuel
   b. Flue gas temperatures of 400°F to 500°F
   c. SO_2 emissions
   d. Lubricating impurities
   e. None of the above

References

---

[1] Keating, L.E. 1993. *Applied Combustion*. Marcel Dekker, Inc. New York, NY.

[2] Obert, E. F. 1973. *Internal Combustion Engines and Air Pollution.* Harper & Row, Publishers, Inc. New York, NY.

[3] Pilat, M.J. *Combustion Evaluation in Air Pollution Control.* APTI Course 427. Department of Civil Engineering. University of Washington.

[4] Cooper, C.D., and F.C. Alley. 1994. *Air Pollution Control: A Design Approach*. Waveland Press, Inc. Prospects Heights, IL.

[5] Pulkrabek, W.W. 1997. *Engineering Fundaments of the Internal Combustion Engine.* Prentice Hall. Upper Saddle River, NJ.

10 Gas Turbines

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Explain the progression of the development of NO_X controls for gas turbines.
2. Explain the operating principles of gas turbines.
3. Name the four general categories of gas turbines.
5. State the difference between firing temperature and flame temperature.
6. Explain how the type of fuel impacts NO_X emissions from gas turbines.
7. Identify the NO_X control techniques that are included in the category of combustion modifications.
8. Explain wet control for gas turbines and identify the various parameters that define the mechanical limits of wet control.
9. Explain dry control for gas turbines and name three dry control techniques.
10. Identify the post-combustion control techniques applicable to gas turbines.
11. Identify the factors that influence the performance of an SCR system in a gas turbine.

10 Gas Turbines

10.1 INTRODUCTION

Gas turbines are combustion systems that generate hot combustion gases that are used for driving a turbine to produce electrical power. They are fired primarily with natural gas, kerosene, and No. 2 (diesel) fuel oil. Gas-turbines are stationary power and energy generating systems that were originally developed from aircraft jet engines.

Gas turbines are used for the generation of emergency electrical power, the generation of electricity to meet peak power demands, the powering of pumps and compressors in remote locations (i.e., pipelines) and the generation of electrical power and steam for industrial facilities. Power outputs range from 300 horsepower (hp) for small units to over 250,000 hp for large units.

Thermal NO_X formation is responsible for the majority of NO_X emissions from gas turbines. The nitrogen levels in the fuels appropriate for gas turbines are too low to contribute substantially to fuel NO_X formation. Prompt NO_X formation in gas turbines can be important because of the very low NO_X emission levels that are required in some systems. Prompt NO_X formation results in NO_X levels less than 10 ppm. The chemical reactions of the prompt NO_X mechanism are *not* strongly dependent on the peak gas temperatures, peak oxygen levels, and gas residence times in peak temperature-oxygen areas.

10.1.1 Development of Control Strategies

The first major gas turbine regulations were included in the Clean Air Act Amendments (CAAA) of 1977. Non-attainment areas for CO and NO_X in 1977 were to achieve attainment by 1987. Gas turbines were required to meet the New Source Performance Standard (NSPS) of 75 ppm for utility sources and 150 ppm for industrial sources (with corrections for heat rates). The NSPS was based on steam injection and water injection controls, termed *wet controls.* Wet controls are combustion modifications that reduces the peak gas temperature in the combustor, thereby reducing NO_X formation.

EPA considered water or steam injection to be the best achievable control technology (BACT) during the late 1970s and early 1980s.

However, by the end of 1987, EPA promulgated the top-down approach to determining BACT, and NO_X emissions from gas turbines began decreasing. The trend has been a steady decrease in NO_X emissions from gas turbines since the NSPS was originally promulgated in 1980.

Uncontrolled NO_X emissions from gas turbines range from 150 to 250 ppm. The use of steam and water injection reduced these levels to the 75 ppm level required by the NSPS.

In the mid-1980s, multi-nozzle combustors were installed on gas turbine units. Multi-nozzle technology reduced NO_X emissions for gas-fired units to approximately 25 ppm and to approximately 42 ppm for oil-fired units. This was a *mechanical* change, and it prevented water and steam injection from achieving additional NO_X reductions.

In the mid-1980s selective catalytic reduction (SCR) technology was first applied to gas turbines in the U.S. SCR systems are add-on control systems capable limiting NO_X emissions to less than 10 ppm. In response to this technology, the State of California began requiring gas turbines to meet a 10 ppm limit.

In the late 1980s and early 1990s, lean pre-mix designs and staged lean pre-mix designs (termed *dry controls*) were implemented on gas turbines. These combustion modification techniques reduced NO_X emissions from 25 ppm to less than 10 ppm for gas-fired turbines.

The key regulatory driver in attainment areas was BACT and LAER and offsets in non-attainment areas. These drivers have prompted manufacturers to develop turbine designs that lower NO_X emissions without add-on controls.

New control strategies such as catalytic combustion and $SCONO_X$ demonstrate the potential for even lower emissions levels. However, further testing on gas turbines is necessary for these control options to become widely accepted.

10.1.2 Gas Turbine Characteristics

Gas turbines were initially developed for use in jet aircraft engines. They consist of three major components: the compressor, the combustors, and the power turbine. Air is adiabatically compressed to approximately 30 times ambient conditions in the compressor prior to ignition in the combustor. The air and fuel are burned in the combustors at the elevated pressure. After exiting the combustion zone, the exhaust gas expands and cools, transferring energy to a rotating shaft in the form of mechanical work.

In jet engine applications, these hot gases provide the thrust to power the airplane.

> More than 50% of the mechanical work drives the compressor, and the balance of recovered work is used for power generation.

The basic turbine components are shown in Figure 10-1.

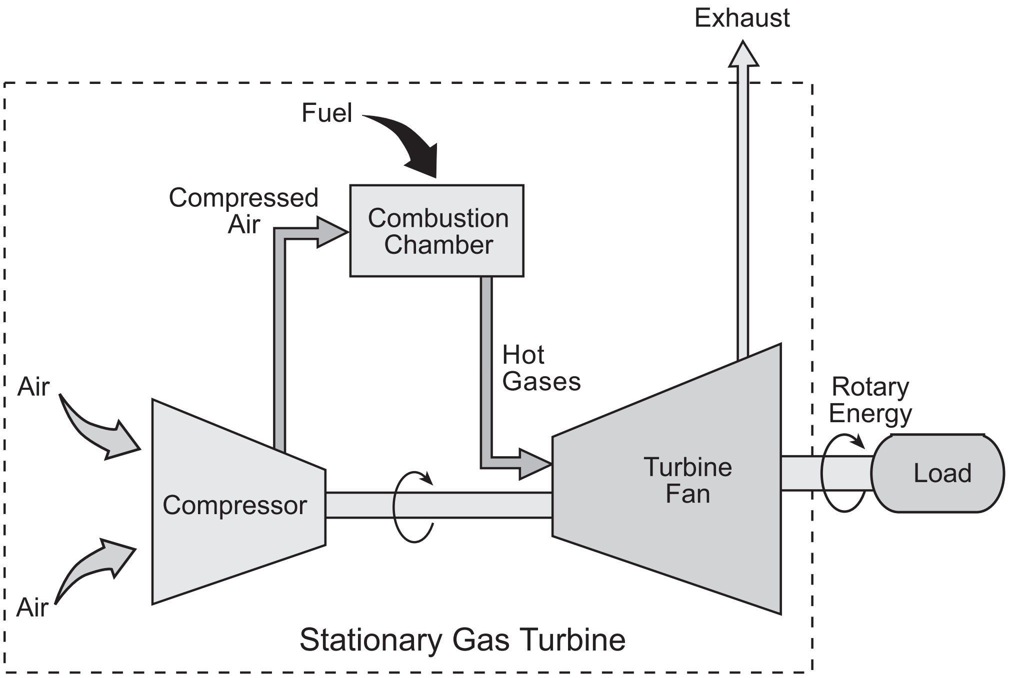


Figure 10-1. Basic schematic of a simple cycle gas turbine

There are four general categories of gas turbines. They are classified based on the extent to which additional energy is recovered from the hot exhaust gases.

1. **Simple cycle**. Exhaust gases are released with no heat recovery.
2. **Combined cycle**. Heat is recovered to produce steam for a steam turbine Rankine cycle (with or without supplemental firing)
3. **Regenerative**. Heat is recovered by a heat exchanger to preheat the combustion air.
4. **Cogenerative**. Heat is recovered in a heat recovery steam generator to produce steam for the process (with or without supplemental firing).

Figure 10-1 is an example of a simple cycle gas turbine. A generator is added to the turbine to generate electrical power. The hot exhaust gas stream is exhausted to the atmosphere without any attempt to recover a portion of the remaining heat value.

A schematic of a combined cycle gas turbine system is illustrated in Figure 10-2. In this case, the hot exhaust stream from the gas turbine is used in a heat recovery steam generator (HRSG). The steam is used to generate additional electrical power. In these types of systems, approximately two-thirds of the energy is used in the gas turbine and one-third is used in the steam turbine.

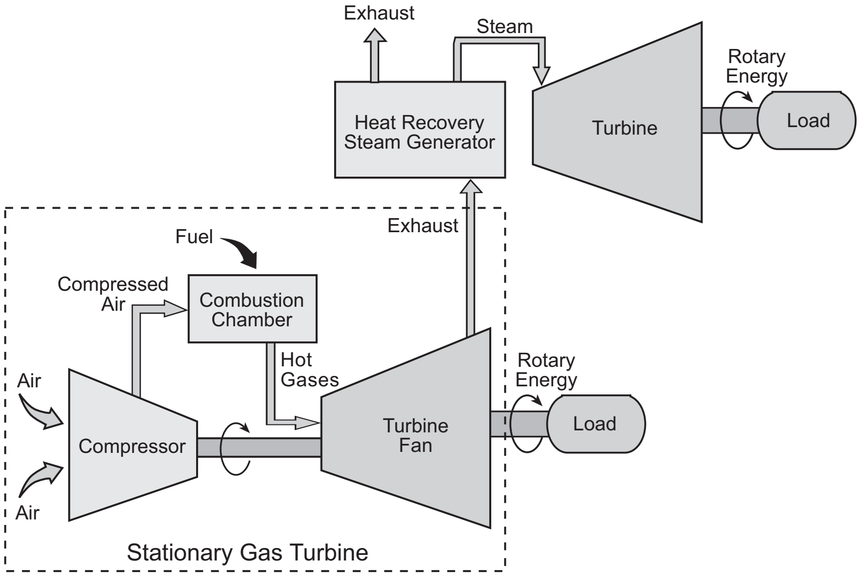


Figure 10-2. Basic schematic of a combined cycle gas turbine

In a regenerative system an indirect heat exchanger is used to transfer sensible heat from the gas turbine exhaust gas stream to the combustion air for the combustors.

A cogeneration system is similar to the combined cycle unit. A part of the system is used directly in the process rather than generating electrical power in a steam turbine.

The thermal efficiency is a useful measure of the extent of heat recovery in the overall gas turbine system. The thermal efficiency is the ratio of useful shaft energy to the fuel energy input. The shaft energy is used to drive the compressor and provide recoverable work. The thermal efficiencies for the four categories of gas turbines are shown in Table 10-1.

Table 10-1
Thermal Efficiencies

Gas Turbines	Thermal Efficiency (% of Fuel Lower Heating Value)
Simple Cycle	15 to 42
Combined Cycle	35
Regenerative Cycle	38 to 60
Cogeneration	up to 84

10.1.3 Combustion

The ratio between the quantity of fuel-fired and the amount of combustion air provided is important in all combustion systems, including gas turbines. The theoretical amount of air necessary for complete combustion of a quantity of fuel is defined as the *stoichiometric ratio*. The *equivalence ratio* is defined as 1.0 when the actual air-to-fuel ratio is equal to the stoichiometric air-to-fuel ratio. At an equivalency ratio of 1.0, a maximum flame temperature is reached and the production of NO_X is maximized.

Firing temperature is the temperature at the entrance to the first stage of the turbine section of the gas turbine. The *flame temperature* is the temperature in the combustor section of the gas turbine.

Firing temperature is an especially important design value for gas turbines, because it directly influences the overall thermal efficiency of the unit. However, flame temperature is limited by the temperature that the materials in the turbine are able to withstand. In order to increase cycle efficiency, gas turbines have been designed for progressively higher firing temperatures. The general ranges are classified in accordance with a simple alphabetic sequence and most modern gas turbines are in the E- or F-series. E-technology turbines operate with a firing temperature of approximately 2020°F. F-class turbines operate with higher combustor pressures and firing temperatures of 2300°F to 2400°F.

Operating a gas turbine at the highest firing temperature will maximize the cycle efficiency. Before regulations focused attention on NO_x emissions controls, gas turbines were designed to operate near ideal stoichiometric conditions. Operating in this manner allowed for stable operating conditions, maximum electrical output, and extended turbine life. Unfortunately the thermal NO_X formation rate is also maximized at this condition.

10.1.4 Control Technologies

There are five basic techniques for controlling NO_X emissions from gas turbines: steam or water injection, SCR, dry low NO_X (or lean pre-mix combustion), catalytic combustion, and $SCONO_X$. These techniques are often used in combination to obtain the lowest achievable NO_X reduction. Table 10-2 provides typical emission levels accomplished with NO_X control techniques.

Table 10-2
Achievable Emission Levels with NO_x Control Techniques

Control Technique	NO_X Emissions, gas-fired turbines (ppm)	NO_X Emissions, No. 2 oil-fired turbines (ppm)
Uncontrolled Emissions	155	240
Steam/Water Injection (Wet Controls)	25	42
Lean Pre-Mix Design (Dry Controls)	9	42
Selective Catalytic Reduction	2-5	4-10
Catalytic Combustion	3	Not applicable
$SCONO_X$	1-3	Not applicable

These control technologies can be categorized as either add-on control technologies or combustion modification technologies. Section 10.2 discusses the combustion modification technologies, and Section 10.3 addresses the post-combustion control technologies.

10.1.5 Fuel Types

The firing and flame temperatures are directly related to the type of fuel-fired in the combustor. The three major types of fuels for gas turbines are natural gas, kerosene (No. 1 oil), and diesel oil (No. 2. oil). The relationship between the firing temperature and fuel type relative to NO_X emissions is illustrated in Figure 10-3.

Fuel oil has a higher flame temperature and produces more NO_X than natural gas. Low-Btu gases, such as synthetic fuels, have very low flame temperatures and produce less NO_X than burning natural gas.

A major consideration of fuel use is the content of sulfur and nitrogen. Sulfur in the fuel results in SO_2 emissions and may corrode components of the gas turbine, especially in conjunction with SCR systems. Nitrogen bound in the fuel will result in fuel NO_X formation. Fuels such as coal-derived liquid, shale oil, and high-nitrogen residual oil are major contributors to fuel NO_X. Because of fuel NO_X formation, these fuels are not commonly used with gas turbines.

Natural gas is a cost-competitive fuel, which is abundantly available. The exact blend of natural gas is regionally variable, and therefore the heating value is also variable. Impurities such as sulfur are minimal for natural gas. The absence of damaging impurities lengthens the life of a turbine. Natural gas, which does not burn as hot as fuel oil, lowers thermal NO_X formation.

Fuel oils are defined as grades No. 1 through No. 6. Lighter fuel oils, called distillate oils, are assigned low numbers and have undergone a more extensive refining process. No. 1 oil and No. 2 oils have low levels of impurities and are used for gas turbines.

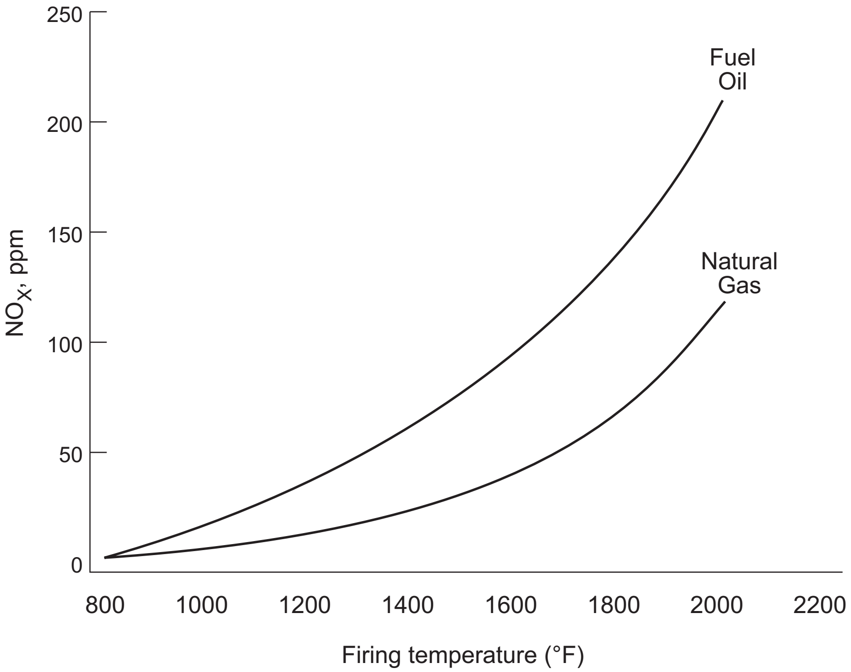


Figure 10-3. Firing temperatures versus relative NO_x emissions for natural gas and fuel oil

Kerosene, No. 1 oil, is used for aircraft derivative gas turbines, also referred to as aero-derivative gas turbines. These are jet aircraft engine designs modified by adding a turbine and generator. The thrust generated by the engine is converted to shaft horsepower by the added turbine. Kerosene has a low sulfur and ash content. Aircraft jet engines are designed for kerosene because of the low levels of impurities such as sulfur and the high heating value. The price of kerosene is relatively high.

Diesel, No. 2 oil, is popular for marine vessels. It is a less expensive fuel and poses a lower threat of explosion during storage. However, sulfur levels are slightly higher than kerosene. The heating value of kerosene and high-grade diesel are similar as shown in Table 10-3. Kerosene and diesel can be used interchangeably without sacrificing engine performance.

Table 10-3
Typical Lower Heating Values and Sulfur Content for Fuels

Fuel	Heating Value kJ/kg	Heating Value Btu/lb$_m$	Sulfur Content % wt.
Kerosene (No. 1 Oil)	43,100	18,500	0.01 to 0.5
Diesel (No. 2 Oil)	42,600	18,300	0.05 to 1.0
Natural Gas	38,000-50,000	16,300-21,500	negligible

NO_X emissions are highly dependent on the thermal NO_X mechanism. Therefore, fuels that burn at a higher flame temperature produce greater NO_X emissions. Other fuels sources have been commercially applied only to a limited number of gas turbine sources. Coal-derived gas (Syngas) and methanol are possible fuel alternatives that burn at lower temperatures.

10.1.6 Combustor Designs

A gas turbine combustor is a device for the continuous mixing and combustion of specified flow of fuel and air. A conventional combustor for a gas turbine is shown in Figure 10-4.

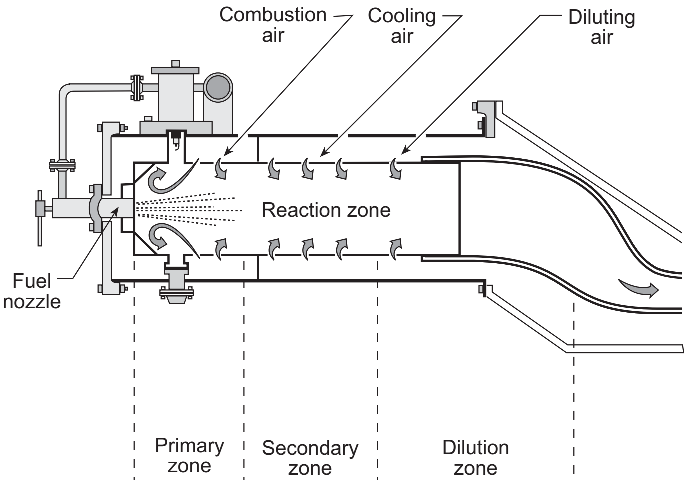


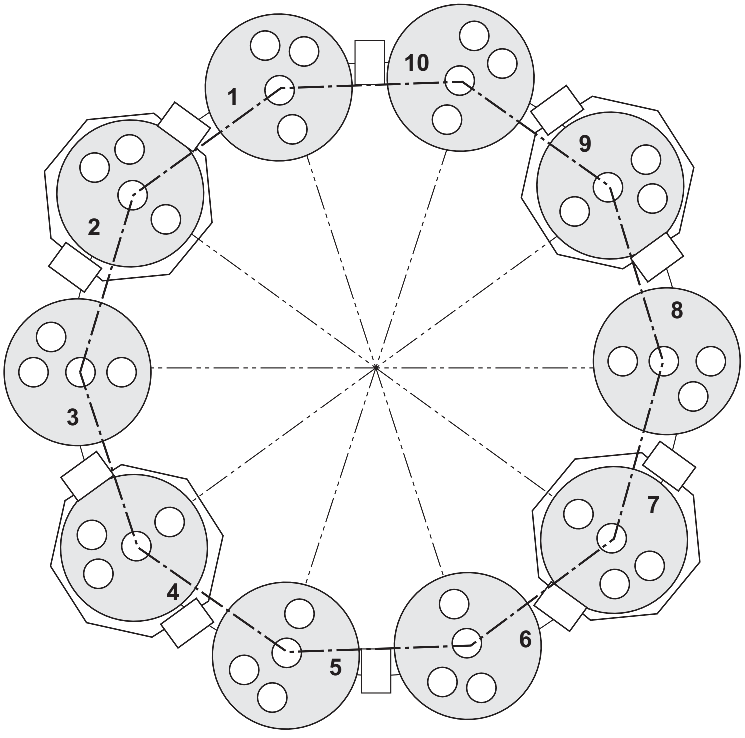
Figure 10-4. Conventional combustor

Combustor designs for gas turbines are either single-pipe, annular, cannular, or silo. All pollutants are generated within the first 10 to 12 inches of the combustor zone of the gas turbine. The hot combustion gases are mixed with air introduced through holes in the chamber. This mixing serves to cool the hot combustion gases that are subsequently passed through a diffuser before going to the turbine.

The single-pipe design simply consists of a single pipe through which air and fuel enter the combustor chamber. In an annular combustor, the fuel and air are injected into the chamber along a continuous outer ring.

In a cannular (reverse-flow) combustor system, the air exits the compressor and turns 180 degrees to flow around the outside of the combustor. The operation of a reverse-flow combustor is similar to operating the single-pipe design: the fuel and air are mixed in the combustion chamber and dilution air is injected in the hot combustion gases before the gases reach the diffuser. Dilution air cools the hot gases to the firing temperature before the gases enter the turbine.

The difference between a cannular combustor and an annular combustor is that, in the cannular design, the air and fuel are injected from *can-shaped* combustors located in the outer ring. A cannular combustor is illustrated in Figure 10-5. Most manufacturers currently use this configuration.



View looking downstream

Figure 10-5. Cannular combustor

The single-pipe, annular, and cannular configurations are applied to smaller gas turbine units. The single-pipe combustor is the simplest and least expensive design. It also creates greater thermal NO_X because of higher flame temperatures. The cannular design has been shown to reduce emissions from 42 ppm (typical of the single-pipe design) to 25 ppm.

The silo design, used for large applications, has large combustor chambers mounted on the outside of the turbine. E-class turbines generally use either a silo or cannular combustor design. The configuration of a silo combustor is similar to the configuration for cannular combustor.

Another type of combustor is used in aircraft derivative engines. These are gas-powered engines that use an annular combustor section. They are jet engines with a generator added to the back end to generate energy.

10.2 COMBUSTION MODIFICATION CONTROLS

10.2.1 Wet Control

The injection of water or steam into the combustor is commonly termed *wet control* for gas turbines. Steam or water injection controls NO_X emissions by decreasing the peak flame temperature. It is employed in combination with other pre-and post-combustion control techniques. Wet control has been successively applied to all types of turbines, except regenerative cycle combustors, for the reduction of thermal NO_X.

During wet control operation, the cycle efficiency is reduced by 2% to 3%, while power output is increased by 5% to 6%.[1] The power increase is a result of a higher mass flow rate due to the water.

Reduction efficiencies of 70% to more than 85% can be achieved with wet control.[2] However, in practice, operating parameters and other emissions must be balanced and 60% to 70% reduction is more typical. Higher reduction efficiencies are experienced with fuel oil-fired combustors than with gas-fired combustors.

Either steam or water is injected with the fuel to reduce peak firing temperatures at typical water-to-fuel ratios of 0.2:1 to 1:1. It is essential that the water used for wet control be free of contaminants. The water should be pretreated to remove minerals and other contaminants that can damage gas turbine components.

Steam injection requires the addition of a steam generating boiler and injection hardware. Water injection requires fewer components and has a greater effect on cooling the firing temperature.

Mechanical Limits

NO_X emissions of 42 ppm for gas-fired turbines and 65 ppm for No. 2 oil-fired turbines are considered to be the mechanical limits. Carbon monoxide (CO) decreases in conjunction with increasing temperature and increasing efficiency of a turbine. As a result, CO is a measure of the inefficiency of the combustion process. Steam or water injection causes the CO levels to increase and the NO_X levels to decrease. Under optimal operating conditions for an E-class turbine, NO_X emissions are 42 ppm.

The following parameters constitute the mechanical limit of gas turbines:

- Combustion dynamic pressure oscillations
- Combustion operating instabilities
- Increased CO
- Heat rate penalty
- Combustion flame blow-off and/or flame-out

Pressure Oscillations and Combustion Noise

Pulsing of the combustor can occur due to pressure oscillations and can damage the combustor and accelerate metal fatigue. Pulsing is a result of high water-to-fuel injection or poor mixing. To help correct for combustion dynamic pressure oscillations and operating instabilities, a multi-nozzle quiet nozzle design was applied to cannular combustors. The multi-nozzle cannular configuration produces better mixing within the combustor. The homogeneous mixture lessens pressure oscillations and results in smoother combustion. Installation of a six-nozzle quiet design can reduce NO_X emissions from 42 ppm to 25 ppm for gas-fired units without dynamic pressure disturbances.

Combustion noise is also reduced with the use of steam, as opposed to water injection. Steam injection produces a more thorough mixing of water with the combustion gases and fuel. This allows for fewer disturbances in the burners and is the generally preferable method of wet control.

Increased CO

As with most NO_X pre-combustion control techniques, use of wet control will increase CO and hydrocarbon emissions.

> CO emissions are increased considerably while the hydrocarbon emission increase is more moderate.

This creates another limit to the water-to-fuel ratio. Water-to-fuel ratios of 1:1 will result in a five-fold increase of CO emissions to approximately 300 ppm.[3]

Heat Rate Penalty

The need to add more energy to heat the steam or water that is added to the system is called the *heat rate penalty*. Heat is transferred to the water or steam that is injected, resulting in the requirement of additional fuel to generate the same amount of power.

Heat loss with the injection of water is higher than steam injection. Additional thermal energy from combustion must be transferred to the water in order to overcome the enthalpy of vaporization.

Flame Blow-Off and Flame-Out
Flame blow-off and flame-out are possible with wet injection. During engine deceleration cycles the combustor is especially susceptible to these problems. Wet injection is often reduced or suspended during these periods.

10.2.2 Dry Control

Increasingly stringent NO_X emission control requirements stimulated research of combustion modification techniques to reduce NO_X emissions below levels achievable by wet techniques. *Dry controls* are performed without the use of water or steam by reducing the flame temperatures and decreasing residence time.

10.2.2.1 Lean Combustion

Lean combustion is accomplished by operating the combustor fuel-lean in order to lower flame temperatures and reduce NO_X. The fuel-to-air ratio is lowered to less than half of the stoichiometric ratio.[4]

Lean pre-mix combustors mix the fuel and air prior to injection. In lean pre-mix combustion, the fuel and air are combined thoroughly to form a very lean mixture before delivery to the combustor. The air-to-fuel ratio is regulated within a small window slightly lower than the design point (i.e., lean flammability limit). The lean pre-mix design is a popular and cost-efficient control option.

> To minimize combustion operating instabilities and CO formation, a pilot flame can be incorporated to complete combustion. NO_X emission levels are guaranteed by manufacturers to be 9 ppm to 25 ppm, depending on the specific gas turbine design.[5]

10.2.2.2 Staged Combustion

Lean combustion is often combined with a staging process. While pre-lean combustion limits the flame temperature, air staging limits the residence time at the peak flame temperatures. Reducing the peak flame temperatures and lowering the residence time are combustion controls for limiting the thermal NO_X mechanism.

> The following four parameters are interrelated and critical to staged combustion: NO_X, dynamics, CO, and turndown. For example, as NO_X levels decrease, CO levels increase. *Turndown* is defined as the ability to operate at reduced loads.

Staged combustion is often called Dry-Low NOx (DLN), Dry-Low Emissions (DLE), or SoLoNOx. Manufacturers use a combination of the two types of staged combustion, fuel staging, and air staging. In staged combustion, the combustion zone is separated into a primary combustion zone and a secondary combustion zone. The primary fuel nozzles are located in a concentric pattern around a centrally located secondary fuel nozzle. The primary combustion zone is formed around the outside of the secondary nozzle and the secondary zone is downstream of the secondary nozzle. Fuel and air are added through the primary nozzles, and only fuel is added through the secondary nozzle. Two-staged lean/lean combustion or two-staged rich/lean combustion are applied for NO_X reduction

Two-Stage Lean/Lean Combustion

In both the primary and secondary zones, the air-fuel mixture is burned fuel-lean. To maintain combustion stability, a pilot flame operating near ideal stoichiometric conditions is maintained. Flame temperature is kept low in both zones.

Two-Stage Rich/Lean Combustion

Rich/lean combustors stage combustion by operating the primary zone fuel-rich and the secondary zone fuel-lean. The fuel-rich zone limits the temperature and oxygen availability for NO_X formation. Combustion is incomplete in the primary zone, and CO and hydrocarbon levels are high. Combustion is completed in the secondary zone, reducing the CO and hydrocarbons. The secondary zone also limits the flame temperature by burning with excess air.

Limiting oxygen in the rich zone is effective in controlling fuel NO_X. Therefore, two-stage rich/lean combustion is a beneficial control option for higher nitrogen fuels such as diesel. Emissions reductions of as much as 50% to 80% can be achieved.[2]

10.2.3 Catalytic Combustion

Catalytic Combustion Systems, Incorporated has developed an alternative technique called the XONON™ process for combustion within gas turbines. The XONON™ system is a catalytic combustion system, which is applicable to diffusion and lean pre-mix combustors. This process minimizes NO_X emissions to as low as 3 ppm by burning the fuel in the presence of a flameless low temperature catalyst. These low NO_X levels are accomplished while limiting CO and unburned hydrocarbons to 10 ppm.

Combustion is accomplished in two steps. Partial combustion takes place within the catalyst at a controlled temperature during which virtually no NO_X formation takes place. Completion of the combustion process is accomplished downstream with a flameless homogeneous reaction. Only small amounts of NO_X are produced in the second combustion step. Although catalytic combustion may become a more popular control technique in the future, there are currently only a few commercial applications.

10.3 POST-COMBUSTION CONTROLS

The dominant post-combustion control system for gas turbines has been selective catalytic reduction (SCR). The following section describes SCR application on gas turbines. A more detailed description of SCR systems is provided in Chapter 11.

Selective non-catalytic reduction systems (SNCRs) are not very compatible with gas turbines for several reasons. The required operating temperature of SNCRs is 1600°F to 1900°F, while the gas exhaust temperatures for gas turbines is less than 1100°F. Also the residence time of the flue gas in the necessary temperature range is longer than available in gas turbines. Other post-combustion systems, such as SCONOx™, are feasible alternatives but have had limited commercial use. SNCR systems are fully described in Chapter 12.

10.3.1 SCR

SCR is a post-combustion technique that was first installed in Japan and was first implemented in the United States in the mid-1980s. In 1985 the South Coast Air Quality Management District (SCAQMD) in California was the first agency to set NO_X emission limits based on SCR technology. SCAQMD permits for gas turbines limited NO_X emissions to 9 ppm. Newly installed SCR systems are capable of reducing NO_X emissions by 80% to 90%. Over time this efficiency is usually reduced slightly.

An SCR system uses ammonia to react with NO_X in a complex set of high-temperature heterogeneous reactions on the surface of a catalyst. A basic illustration of a gas turbine equipped with an SCR system is shown in Figure 10-6. Hot gases pass over a catalyst bed located in the heat recovery steam generator. Ammonia and NO_X react within a specified temperature range to produce nitrogen and water. The reagent (ammonia) is injected into the gas stream upstream of the catalyst bed vessel. A grid of injection nozzles is used to ensure optimal reagent-gas distribution.

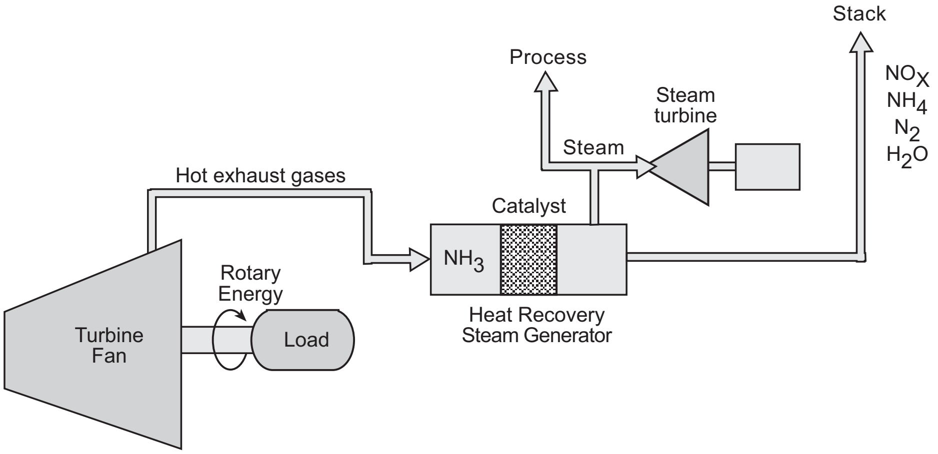


Figure 10-6. Gas turbine equipped with an SCR system

The reaction rate is not 100% efficient and, consequently, the stack gases contain unreacted NO_X, ammonia, molecular nitrogen (N_2), and water vapor. The small quantities of ammonia that remain in the gas stream after the reactions are completed are termed *ammonia slip* emissions.

The SCR system uses a catalyst-impregnated bed to reduce NO_X emissions. By using the catalyst, the activation energy for the chemical reduction reaction between ammonia and NO_X is reduced and occurs at much lower temperatures. Most SCR systems operate in the range of 600°F to 800°F. Temperatures below the operating range result in increased ammonia slip. Temperatures above the operating range may damage the catalyst.

The operating temperature range is important for placement and application of SCR system for gas turbines. SCRs are not desirable for simple cycle gas turbines. The exhaust gas temperature for simple cycle gas turbines is 850°F to 1000°F and 1100°F for an F-class turbine. At these temperatures, additional equipment is necessary to cool the flue gas to the appropriate operating temperature range of the SCR. SCR systems operate best with combined cycle/cogeneration installations.

The SCR is located in the heat recovery steam generator (HRSG). Because of heat transfer by the heat recovery system, temperatures are reduced to suitable levels for SCR operation. The exact location within the HRSG is site-specific.

In addition to the SCR catalyst for NO_X control, some gas turbines also have a separate catalyst bed for CO oxidation to CO_2. The CO catalyst bed is located before the HRSG as indicated in Figure 10-7.

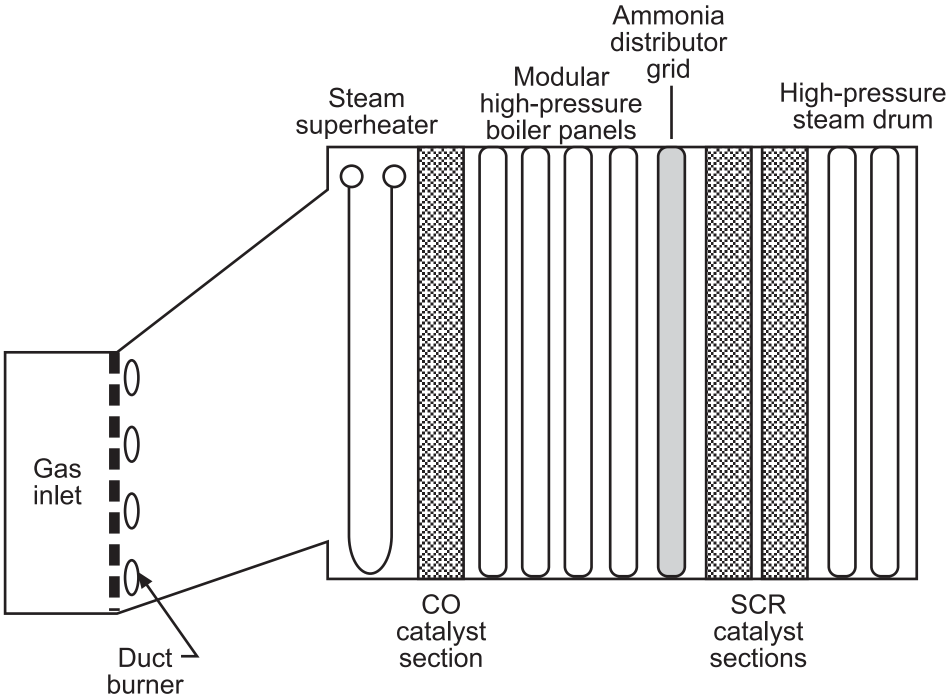


Figure 10-7. CO and SCR catalyst locations in the HRSG

Some manufacturers claim to have developed high-temperature SCR systems. Typically, the exhaust temperature for an E-technology turbine is around 1000°F. In the case of aircraft derivation engines, the exhaust temperature is around 850°F. Therefore, SCR could be used on these systems without the use of HRSG. However, the new F-class turbines have exit temperatures of around 1100°F and there are no SCR systems that can operate at that temperature.

The SCR catalyst is an extruded honeycomb design containing the catalyst material (e.g., vanadium oxide) throughout the entire monolith. Most gas turbines burn low particulate matter-emitting fuels. SCR catalyst designs for these gas turbines can have relatively small pitch due to the low emissions of particulate matter. Pitch refers to the open distance between plates or cells. Smaller pitch allows greater surface contact of the flue gas, but it can restrict the flow rate. Fuels with high ash content can result in fouling of the catalyst.

Experience indicates that SCR works best in base load applications using natural gas. Natural gas contains few or no trace species that can poison the catalyst.

An ultimate analysis should be performed if fuels other than natural gas are used. Alkalis, arsenic, iron, silica, zinc, phosphorus, calcium sulfate, chlorides, and siloxanes are all capable of poisoning, fouling or masking the catalyst.

As with most post-combustion control systems, the use of SCR increases the pressure drop across the turbine, thereby increasing the fuel consumption of the turbine. This increase in fuel consumption results in an increase in emissions.

Increasingly stringent regulation has been the impetus for installation of SCR systems. SCR systems are the only control device that is well proven for a variety of commercial applications to control NO_X to levels less than 10 ppm. However, the systems are complex, associated with high costs, and impose environmental trade-offs. For example, the SCR reduces NO_X emissions, but increases ammonia emissions. Problems that can result from use of SCR include the following:

- ***Ammonia slip/spills.*** Ammonia is not a hazardous air pollutant under Section 112 of the Clean Air Act; however, it is an Extremely Hazardous Substance under the Superfund Amendments and Reauthorization Act (SARA) Title III.

- ***Temperature Dependence.*** The reaction kinetics associated with the use of SCR occurs in a narrow temperature range (600–800°F). Above 800°F, the ammonia oxidizes to NO_X and irreversible damage occurs to the catalyst when vanadium pentoxide is used. At temperatures below 600°F, the ammonia slip increases because the reaction rate decreases substantially.

  Load capability is limited with supplemental firing that produces higher temperatures (1400-1500°F) in the HRSG. As a result, the catalyst must be located on the downstream side (i.e., the low pressure end) of the HRSG.

- ***Sulfur Bearing Fuels.*** Sulfur in the fuels can deactivate some types of catalysts. Sulfur also reacts with the ammonia reagent to cause corrosion and sulfur compound emissions (e.g., SO_2). Resulting ammonium bisulfate accelerates corrosion of the HRSG tubes and can also foul and plug boiler and catalyst surfaces. Ammonium sulfate increases the emissions of fine particulates and regional haze.

- ***Disposal of Spent Catalyst.*** The spent catalyst is a hazardous waste and requires disposal accordingly. The most common catalyst for SCRs is vanadium pentoxide, an Extremely Hazardous Substance under SARA.

10.3.2 SCONOx™

SCONOx™ is a relatively new control technique that controls NO_X emissions with a two-step process on a single potassium nitrate-impregnated catalyst. In the first step, the catalyst oxidizes NO to NO_2 and CO to CO_2. NO_2 is then absorbed onto the treated surface of the SCONOx™ catalyst.

The absorbed NO_2 is periodically removed from the catalyst with dilute hydrogen. As the hydrogen contacts the catalyst in the presence of oxygen, the absorbed NO_2 is converted to nitrogen and water.

The manufacturer guarantees emissions of 2 ppm for NO_X and 1 ppm for CO. Since ammonia is not used as a reagent, many of the problems experienced with SCR systems are eliminated. However, the cost and the pressure drop of a SCONOx™ system are significantly higher than those associated with an SCR system. SCONOx™ is not applicable to units with sulfur-bearing fuels.

> As of 2000, ABB Alstom Power was the only large-scale gas turbine licensee of SCONOx™. After a year-long testing program, ABB Alstom determined SCONOx to be a commercially available control option for large combined cycle gas-fired turbines. EPA Region 1 considers SCONOx™ to be a "technically feasible and commercially available air pollution control technology." In March 1998, EPA Region IX concluded that SCONOx™ had demonstrated NO_X emissions control of 2.0 ppm (at 15% O_2) and was considered to provide the lowest achievable emission reduction (LAER).

Review Exercises

1. Why is natural gas beneficial over distillate oils for gas turbine applications? (Select all that apply.)
   a. Natural gas is lower in sulfur content and other damaging impurities.
   b. Natural gas is a less expensive fuel.
   c. Natural gas is less explosive and easier to store.
   d. Natural gas burns at a lower temperature than fuel oils reducing thermal NO_X.
   e. None of the above

2. What are the benefits of the lean pre-mix combustion? (Select all that apply.)
   a. It is a cost-efficient NO_X control option.
   b. Can be applied in conjunction with post combustion control techniques.
   c. Produces stable combustion operation compared with diffusion combustion.
   d. Reduces CO and unburned hydrocarbons compared with diffusion combustion.
   e. None of the above

3. What are the benefits of wet injection? (Select all that apply.)
   a. The cycle efficiency is increased.
   b. The power output is increased.
   c. Applicable to all gas turbine designs.
   d. Carbon monoxide emissions are decreased.
   e. None of the above.

4. Lean/lean staged combustion limits NO_X emission by the following? (Select all that apply.)
   a. Limiting the available oxygen during combustion.
   b. Limiting the fuel bound nitrogen content.
   c. Limiting the flame temperature.
   d. Limiting the residence time.
   e. None of the above

5. What are the benefits of SCR systems? (Select all that apply.)
   a. Low operating and maintenance costs.
   b. No increase in other emissions.
   c. Applicable to all gas turbine designs.
   d. Simple to install and operate.
   e. None of the above

6. What are the benefits of the multi-nozzle, quiet-nozzle design? (Select all that apply.)
   a. Provide better combustion stability.
   b. Reduces pressure oscillations.
   c. Increases the life span of turbine components.
   d. Reduces NO_X emissions.
   e. None of the above.

7. When were SCR systems first applied to gas turbines in the U.S.?
   a. Mid 1970s
   b. Mid 1980s
   c. Mid 1990s
   d. 1995
   e. None of the above

8. What is the approximate maximum pressure inside the combustor? (ambient pressure = 1 ATM)
   a. 0.033 ATM
   b. 0.5 ATM
   c. 3 ATM
   d. 30 ATM
   e. None of the above

9. SCR works best in which temperature range?
   a. 600°F to 800°F
   b. 850°F to 1000°F
   c. 1000°F to 1100°F
   d. 2300°F to 2400°F

10. Which of the following control techniques utilizes a catalyst? (Select all that apply.)
    a. Lean Pre-Mix
    b. SCR
    c. XONON™
    d. SCONOx™
    e. None of the above

References

---

[1] Barboxa, M. J., M. J. Cannon, N. J. Charno, and P.S. Oliver. 2000. *Air and Waste Engineering Manual*. John Wiley & Sons. New York, NY.

[2] U.S. Environmental Protection Agency. February 1992. *Summary of NO_x Control Technologies and their Availability and Extent of Application*. EPA-450/3-92-004.

[3] U.S. Environmental Protection Agency. July 1986. *Nitrogen Oxide Control for Stationary Combustion Sources*. EPA/625/5-86/020.

[4] U.S. Environmental Protection Agency. April 2000. EPA AP-42 Document, Fifth Edition, Volume 1 Chapter 3 Supplement F.

[5] Solt, J.C. and M. Schorr. March 1998. *Gas Turbine NO_X Emission Control.* ICAC Foram. Durham, NC.

11 Selective Catalytic Reduction

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Explain the operating principles of selective catalytic reduction.
2. Name the options for locating SCR systems in electric generating units.
3. Identify the components of an SCR reagent injection system.
4. Calculate the reagent feed rate based on the stoichiometry of the conversion reactions and the required outlet concentration.
5. Identify the physical characteristics of catalysts used in SCR systems.
6. Describe the mechanisms by which the SCR catalyst works.
7. Identify the factors that influence the performance of an SCR system.
8. Identify the instrumentation used on SCR systems.

11 Selective Catalytic Reduction

11.1 INTRODUCTION

Selective catalytic reduction (SCR) was first patented in the U.S. in 1957 well before environmental regulations required SCR technology.[1] With the development of a vanadium/titanium catalyst that can withstand both the dynamic environment and temperature range associated with a utility boiler, SCR became a commercially viable technology. SCR was successfully applied to gas-fired units during the mid-1970s and coal-fired units in the 1980s. These early installations were located in Japan and Western Europe.

SCR was first implemented in the United States on gas turbines in the mid-1980s. Today SCR systems are being used for numerous gas turbines and a growing number of coal- oil-, and gas-fired boilers in the U.S.

> Concerns regarding the detrimental effects of U.S. coals on the catalyst and downstream equipment delayed the application of SCR systems to coal-fired units.[1] SCR systems were first installed on coal-fired units in the U.S. in 1994 and are proving to be successful.

In Europe, SCR systems have successfully complied with NO_X emission limits that range from 0.93 lb/MMBtu to 0.08 lb/MMBtu. By comparison, the Phase II NO_X limits for utilities under the acid rain requirements are 0.86 lb/MMBtu for cyclonic units and 0.4 lb/MMBtu for tangentially-fired units. The NO_X SIP Call will require electric generating units in the affected states to meet an emission limit of 0.15 lb/MMBtu by the year 2003.

> Most combustion systems are unable to meet this level without post-combustion control equipment.

It is expected that SCR will become a more widely used post-combustion control technology for NO_X in the U.S.

> When properly designed and operated, SCR systems are capable of sustaining NO_X reductions in the range of 50% to 90%. The actual NO_X reduction efficiency is partly dependent on the initial NO_X levels prior to SCR installation. Reduction efficiencies of 50% to 70% are more common for processes with pre-existing combustion control techniques.

To minimize reagent costs, SCR systems are applied after all reasonable combustion modifications have been installed in the boiler to reduce the NO_X formation rates.

Limitations of SCR systems are discussed in Section 11.3. Some of these limitations are disposal of the spent catalyst, high capital and operating costs, and the complexity of the system. Spent catalysts are designated as hazardous materials, therefore disposal requirements are strict. Capital costs are high because of the large-scale vessels needed to house the catalyst beds and the cost of the catalyst modules themselves. Operating costs for SCR systems are as high as other types of add-on NO_X control systems due, in part, to the cost of the ammonia reagent to react with the NO_X. The system complexity results from the need to maintain the necessary ammonia-NO_X stoichiometric ratios and to protect the catalyst from conditions that could reduce activity.

This chapter focuses primarily on the application of SCR to coal-fired electric utility units. Applicability of SCR systems to gas turbines was presented in Chapter 10.

11.2 OPERATING PRINCIPLES

In an SCR system, the hot exhaust gas stream from the combustion process is cooled to a temperature range of 550°F to 800°F (288°C to 427°C) in the heat exchange areas of the boiler. Downstream of the economizer, ammonia-containing air or steam is injected through a series of nozzles arranged in a grid to facilitate uniform mixing prior to the catalyst bed. Ammonia reduces the nitrogen oxides to nitrogen and water vapor on the catalyst surface in a complex set of high temperature, heterogeneous gas-phase reactions.

The effluent gas stream leaving the SCR system contains the unreacted NO_X and small quantities of ammonia. Ammonia (NH_3)emissions are generally termed *ammonia slip*.

Ammonia slip is reagent that has passed through the catalyst without participating in chemical reactions. Ammonia concentrations greater than 20 ppm can be objectionable in some cases because ammonia can form a light-scattering particulate matter plume by reacting with hydrogen chloride and/or sulfuric acid.

Reactions 11-1 and 11-2 display the overall NO_x reduction reactions that are the basis for SCR technology. These reactions summarize the result of a number of separate reactions on the SCR catalyst surface.

$$4NH_3 + 4NO + O_2 \longrightarrow 4N_2 + 6H_2O \qquad \text{Reaction 11-1}$$

$$4NH_3 + 2NO_2 + O_2 \longrightarrow 3N_2 + 6H_2O \qquad \text{Reaction 11-2}$$

The activation energies for the above reaction processes are greatly reduced with the use of the catalyst. The maximum rate of conversion for Reactions 11-1 and 11-2 occurs at 650°F to 750°F in the presence of a catalyst, compared with 1,600°F to 1,900°F without a catalyst. Therefore, the SCR system is installed at a location downstream of the boiler furnace and some of the boiler heat exchange equipment.

The introduction of a catalyst also allows undesirable side reactions to occur. For instance, a small portion of sulfur dioxide (SO_2) in the flue gas may be oxidized to sulfur trioxide (SO_3) as shown in Reaction 11-3.

$$2SO_2 + O_2 \xrightarrow{\text{catalyst}} 2SO_3$$ Reaction 11-3

SO_3 from the above reaction can then react with ammonia. Consequently ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($[NH_4]_2SO_4$) can form, as shown in Reactions 11-4 and 11-5.

$$SO_3 + NH_3 + H_2O \longrightarrow NH_4HSO_4$$ Reaction 11-4

$$SO_3 + 2NH_3 + H_2O \longrightarrow (NH_4)_2SO_4$$ Reaction 11-5

Ammonium sulfate compounds are capable of corroding and plugging downstream equipment. NH_4HSO_4 and $(NH_4)_2SO_4$ form sticky deposits, which can restrict gas flow and result in very expensive unscheduled maintenance. The corrosive nature of NH_4HSO_4 can damage downstream equipment, such as the air preheater. To avoid problems with NH_4HSO_4, the SCR system must operate above the temperature where this compound forms. Catalysts used on coal-fired boilers have been formulated to minimize the generation of SO_3.

$(NH_4)_2SO_4$ homogeneously and heterogeneously nucleates to form fine particulate matter. Homogeneous nucleation is the formation of new particles composed almost entirely of the vapor phase material. Formation of particles by homogeneous nucleation involves only one compound. Heterogeneous nucleation is the accumulation of material on the surfaces of existing particles, thereby creating particles of more than one compound. These reactions are often indicated by plume formation when the flue gases enter the atmosphere. In addition to forming ammonium sulfates, the sulfur trioxide can react with water vapor to form sulfuric acid, which condenses and corrodes downstream equipment. Catalyst composites dictate the high end of the operating temperature range. Presently available catalysts that operate at temperatures greater than 850° F may actually create NO_X with NH_3 reactions on the catalyst surface. NH_3 is oxidized to form NO, as shown in Reaction 11-6.

$$4NH_3 + 5O_2 \xrightarrow{>850\ ^\circ F} 4NO + 6H_2O$$ Reaction 11-6

NO_X reduction efficiencies ranging from 50% to 90% are possible when the following conditions are met:

- The amount of catalyst is sufficient
- The catalyst is in good condition
- The ammonia reagent flow is sufficient
- The ammonia is adequately distributed across the gas stream

With moderate-to-high inlet NO_X levels, reduction efficiencies of 70% to 90% can be sustained, provided that those conditions are met.

11.3 SCR CONFIGURATION

Because of SCR temperature requirements, correct placement of the SCR system in the process is important. The following sections describe three options for placing an SCR system at electric generating units.

11.3.1 High Dust System

In a high dust system, the SCR is located upstream of the air preheater, particulate matter control equipment, and SO_2 control equipment (i.e., FGD). This location is the most popular because flue gas temperatures are ideal for NO_X decomposition.[2] A simplified flow diagram of the high dust system is displayed in Figure 11-1.

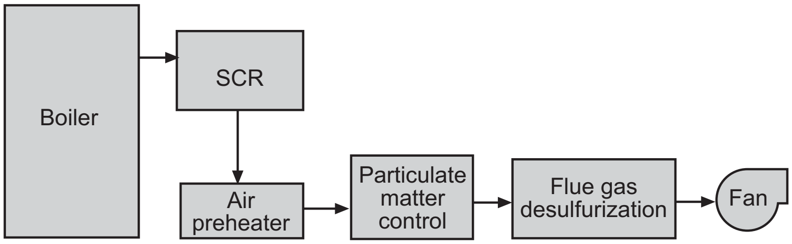


Figure 11-1. High dust system

Locating the SCR system immediately downstream of the boiler reduces capital costs because reheating flue gas stream is not required.

Moderate ammonia slip levels can have a beneficial effect on fly ash resistivity and thereby improve the operation of electrostatic precipitator particulate matter control systems downstream from the SCR system.

The catalyst is, however, susceptible to fly ash buildup and deactivation because it is located before the particulate matter and SO_2 control equipment. Another potential disadvantage of the high dust system is contamination of the fly ash by the reagent.

To reduce operating costs, fly ash is sold to Portland cement and asphalt concrete manufacturers for use as product. The salability of the fly ash is greatly reduced by the presence of adsorbed ammonia. The loss of fly ash revenue, coupled with the cost of ash disposal, will increase SCR system operating costs.

In addition, the formation of ammonium sulfate compounds (Reactions 11-3 through 11-5) may lead to corrosion, plugging and fouling of the air preheater and other process equipment.

11.3.2 Low Dust System

The low dust system is illustrated in Figure 11-2. In this system the SCR is located where flue gas temperatures are still high and the gas stream has passed through a particulate matter control device.

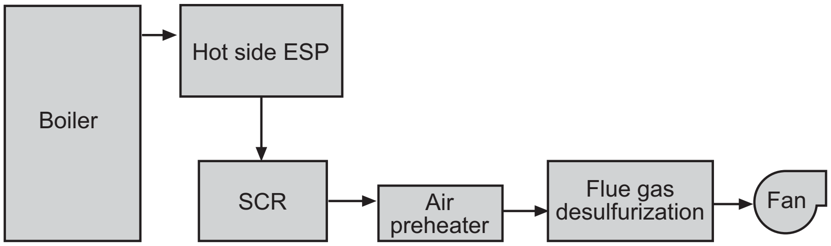


Figure 11-2. Low dust system

With fly ash removal occurring upstream of the SCR, fly ash contamination by the reagent is less likely to be an issue.

Unless a hot side ESP is used, the flue gas has been cooled below 550°F after passing through the particulate matter control device; therefore it must be reheated. The capital cost of installing a low dust system is considered moderate. Potential ammonium sulfate and ammonium bisulfate problems still exist with the low dust system.

11.3.3 Tail End System

The tail end system (shown in Figure 11-3) is not a common configuration on coal-fired boilers. It is generally employed when space constraints make it the only viable option.

The advantage of the tail end system is that flue gas stream is free of both SO_2 and particulate matter, and there is low potential for fly ash deactivation of the catalyst or contamination of fly ash by ammonia. This will help to lengthen the life of the catalyst and downstream equipment and reduce maintenance costs.

Reheating of the flue gas is required with this configuration. Operating and capital costs are therefore higher than the other SCR configurations.

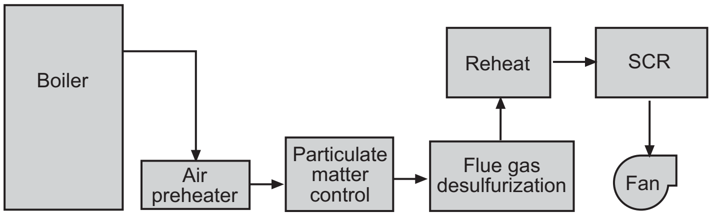


Figure 11-3. Tail end system

Note: The broadcast video segment associated with this chapter includes a narrated video on an SCR installation at a 200 MW power plant. Classroom presentation of this course will also introduce this film segment.

11.3.4 System Components

Figure 11-4 shows an example of an SCR system with aqueous ammonia for a high dust application. This figure displays only the section of the boiler system from the economizer to the air preheater.

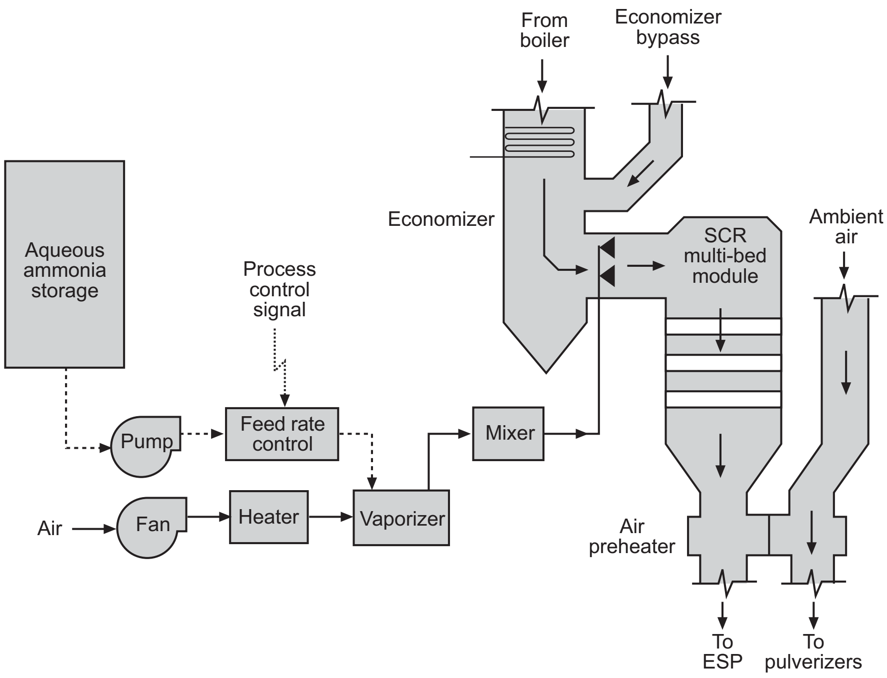


Figure 11-4. Example of an SCR system

The SCR unit is located after the economizer outlet of the furnace. The SCR reactor has three catalyst layers. It is common to leave one of these catalyst layers empty at initial startup so new catalysts can be added as part of the catalyst management plan. In some installations soot blowers may be installed to clean the upper layer of catalyst.

SCR systems commonly have a bypass duct for diverting the flue gas stream when process conditions are not appropriate for SCR operation. Abnormal process conditions or startup and shutdown result in temperature swings. The catalyst is designed and positioned only for normal operating conditions.

The aqueous ammonia injection system is located prior to the reactors and contains heating elements, air fans, mixing chambers, and the injection system. The reactor shown in Figure 11-4 is the common downward vertical flow design, but horizontal and upward flow reactors are used in some installations.

11.4 REAGENT (AMMONIA) INJECTION SYSTEM

Anhydrous or aqueous ammonia is used as a reagent in SCR systems. Both forms of ammonia react similarly when in the gas stream. However, the manner of storage and vaporization is specific to the form of ammonia. For example, anhydrous ammonia is very volatile and requires pressurized storage, while aqueous ammonia does not require pressurized storage. Also, anhydrous ammonia is more concentrated than aqueous ammonia and must be diluted prior to injection.

The reagent system typically consists of the following components:

- Storage tank
- Vaporizer
- Loading/unloading compressors
- Dilution equipment
- Piping
- Flow control and emergency shut-off valves
- Injector nozzles
- Instrumentation

11.4.1 Storage

Anhydrous ammonia is a volatile gas and is usually stored as a pressurized liquid. Release of ammonia gases poses a fire and health hazard. For safety purposes new fire codes require the use of ammonia detectors and emergency scrubbing systems. Aqueous ammonia can be used instead of ammonia gas when there is concern about ammonia gas release from the storage area.

11.4.2 Vaporization and Dilution

A vaporization system maintains a designated vapor pressure in the ammonia tank. Whenever the vapor pressure of the tank decreases below the setpoint, a vaporizer is automatically initiated to increase the vapor pressure to the designated level. Ammonia may be vaporized with electric heat, hot steam, or flue gas recirculation.

The vapor pressure of liquid-phase ammonia can be increased by applying heat with electric coils located in the liquid or by introducing hot air or steam with a forced draft fan. Flue gas can be used to vaporize the ammonia, but this is a less common technique usually reserved for wet-bottom boilers.

Following vaporization, the reagent is metered into a dilution carrier gas stream to keep the ammonia concentration below the explosive range and to facilitate mixing into the gas stream. Air dilution fans send air through an orifice plate to a mixing chamber. The ammonia concentration of the gas stream injected upstream of the SCR bed is usually 3% to 5% by volume.

11.4.3 Ammonia Injection

Once diluted, the vaporized reagent is injected into the gas stream upstream of the catalyst bed vessel. *Direct* or *indirect injection* may be used to introduce ammonia into the flue gas stream. In indirect injection, the ammonia is mixed with the hot air, vaporized and diluted prior to injection. In direct injection, the ammonia is injected directly into the flue gas. The heat of the flue gas vaporizes the ammonia as it leaves the injection nozzles. Aqueous ammonia may be injected directly or indirectly into the flue gas stream; anhydrous ammonia is injected only indirectly.

Injection is accomplished through a series of injection pipes positioned in a grid formation perpendicular to the flow rate and upstream of the catalyst. Grid layout is to promote good mixing of ammonia and flue gas and even distribution across the duct. Control of the each individual injection pipe allows for better control of injection rates. Careful monitoring and adjustment of injection are necessary for optimal NO_X degradation with minimal ammonia slip. The location of reagent injection must allow for adequate residence time prior to catalyst contact. Also, ammonia must be injected at a location where the temperature is below 850°F. If the temperature is greater than 850°F, the ammonia will react with the available oxygen to produce NO_X.

Installing a measurement grid at the catalyst exit is a timesaving and accurate strategy for controlling ammonia injection.[3] The injection rate of each pipe can be adjusted to achieve the associated exit NO_X concentration.

Automatic shut-off valves allow the injection to be suspended during potentially dangerous situations. Detection of high ammonia-to-air ratios or low flue gas flow rates triggers the shut-off valve to close.

The goal is to inject adequate ammonia into the reactor to remove the NO_X. However, if too much ammonia is injected it will pass unreacted through the reactor and result in ammonia slip.

Ammonia slip from SCR systems is usually less than 3 to 5 ppm.[4] The emission of ammonia increases during load changes because of instability of the temperature in the catalyst bed. Ammonia slip can also increase at low loads because of the low gas temperature.

Excess ammonia also contributes to the formation of fly ash, ammonium bisulfate, and ammonium sulfate.

11.4.4 Feed Requirements

Ammonia feed requirements of a nitrogen oxides control system can be estimated based on the stoichiometry of the conversion reactions and the necessary outlet concentration.

Since NO is the dominant form of NO_X in the flue gas, Reaction 11-1 provides the main reaction involved for NO_X removal. This reaction indicates that a theoretical NH_3:NO_X molar ratio of 1.0:1.0 is necessary for NO_X removal. Actual feed requirements differ because of factors such as imperfect mixing, incomplete catalyst surface contact, and limited residence time.

A NO_X reduction of 90% is achievable with a molar ratio of 1.0:1.0 to 1.05:1.00. However, unacceptable ammonia slip of > 20 ppm can result at this molar ratio.[5]

Ammonia is typically injected at stoichiometric ratios of approximately 0.85:1.00[3] to 0.90:1.00[6] to maintain low ammonia slip levels. This means that approximately 0.9 moles of ammonia is needed for every mole of NO_X that must be reduced in order to achieve the emission limitation. Figure 11-5 displays the ammonia feed rates associated with NO_X reduction efficiencies.

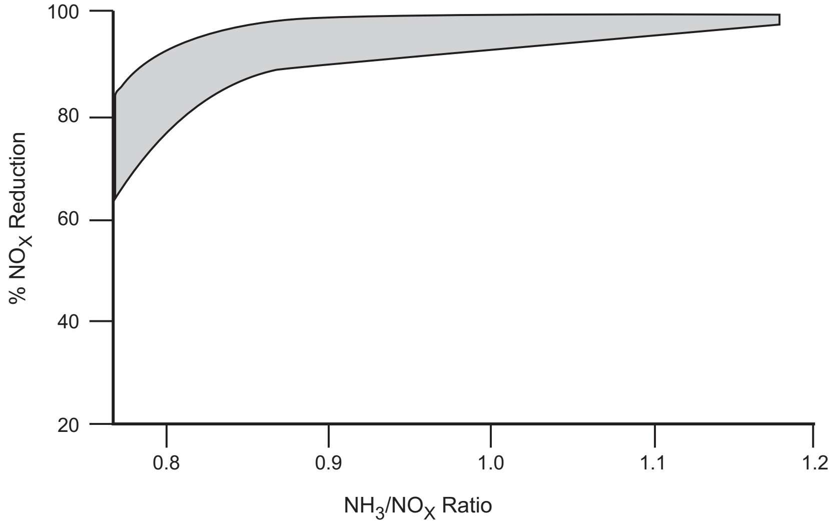


Figure 11-5. Reagent feed rates relative to NO$_x$ efficiency

Problem 11-1

Calculate the ammonia feed rate needed per day to achieve a 60% reduction in the NO$_X$ rate of an SCR system. The boiler flue gas flow rate is 100,000 SCFM and the uncontrolled NO$_X$ emissions rate is 200 ppm.

Step 1. Calculate the pound moles of gas.

$$\frac{100{,}000\text{ scf}}{\text{min}}\left(\frac{\text{lb mole}}{385.3\text{ scf}}\right) = 259.5 \text{ lb moles gas/min}$$

Step 2. Calculate the pound moles of NO$_X$ at uncontrolled conditions.

$$\frac{0.0002\text{ lb moles NO}_x}{\text{lb moles gas}}\left(\frac{259.5\text{ lb moles gas}}{\text{min}}\right) = 0.0519 \text{ lb moles NO}_X\text{/min}$$

Step 3. Calculate the pound moles of NO$_X$ to be reduced.

$$0.6\left(\frac{0.0519\text{ lb moles NO}_x}{\text{min}}\right) = 0.0311 \text{ lb moles NO}_X\text{/min}$$

Step 4. Calculate the pound moles of NH$_3$ required.

$$\frac{0.9\text{ lb moles NH}_3}{1\text{ lb moles NO}_x}\left(\frac{0.0311\text{ lb moles NO}_x}{\text{min}}\right) = 0.028 \text{ lb moles NH}_3\text{/min}$$

Step 5. Calculate the NH_3 of feed per day.

$$\frac{0.028\ \text{lb moles NH}_3}{\text{min}}\left(\frac{17\ \text{lb}_\text{m}}{\text{lb moles NH}_3}\right)\left(\frac{1440\ \text{min}}{\text{day}}\right) = 685\ \text{lb}_\text{m}\ \text{NH}_3/\text{day}$$

11.5 CATALYST

The term *catalyst* refers not only to the active components where NO_X reduction reactions occur, but also the inert substrate form. SCR catalysts are composed of a ceramic material and the active components. The gas stream passes through the channels in the catalyst and the NO_X reduction reactions occur at active sites on the surface or in the pre-structure. There are usually two or three separate catalyst beds in series that are generally replaced one at a time over a multi-year operating period.

11.5.1 Material

Typical catalyst materials include vanadium pentoxide (V_2O_5), titanium dioxide (TiO_2), noble metals, and tungsten trioxide (WO_3).[8] Typically TiO_2 is used as the inert substrate material with V_2O_5 as the active catalyst compound.[1] TiO_2/ V_2O_5 catalysts are resistant to SO_X poisoning.[7] Noble metals are also used as the active catalyst substance.

The catalyst must be selected to minimize the conversion of sulfur dioxide to sulfur trioxide. WO_3 is added to the catalyst formulation to inhibit SO_2 oxidation and increase thermal stability.

Each of the catalysts has a relatively narrow temperature *window*, or range, for efficient operation. Variations of as little as plus or minus 50°F (28°C) from the optimum temperature could have an impact on the NO_X reduction efficiency.[3] Zeolites can be capable of operating at temperatures as high as 1,100°F (593°C).[7] Over 100 high-temperature units have been installed in Europe (EPA 453/R-94-038).[8]

Efforts have also been made to develop catalysts capable of operating at temperatures below 550°F. Low-temperature catalysts are not currently in commercial use.

11.5.2 Physical Characteristics

Catalysts are either homogeneous or heterogeneous composites. Homogeneous catalysts are formed by mixing active substances and substrate material prior to formation. Active substances are therefore incorporated throughout the entire catalyst support material.

Homogeneous catalysts are formed into honeycomb structures. They are beneficial because active substances are still exposed to the gas stream after loss of the outer layer by attrition.

Heterogeneous catalysts consist of a substrate support material (usually a metal or ceramic material) coated with the active components. The physical structure of heterogeneous catalysts can be honeycomb or plate. Figure 11-6 displays the two common physical forms of SCR catalysts.

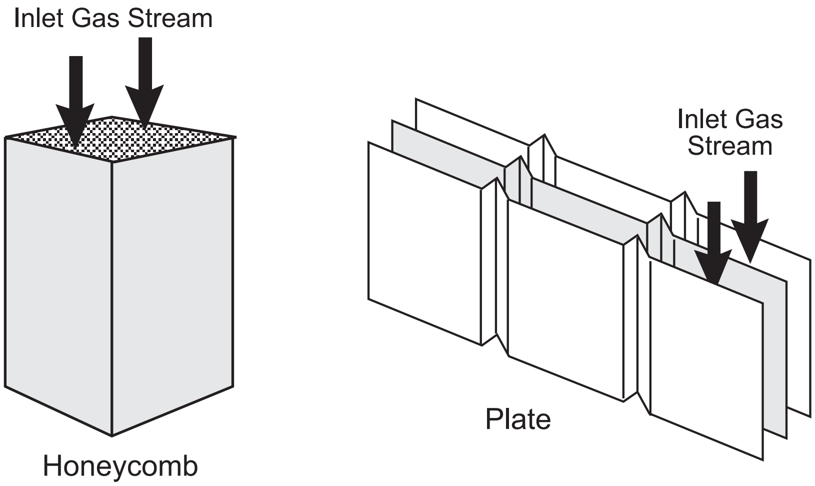


Figure 11-6. Common types of catalysts

Catalyst beds are usually constructed in a honeycomb-type block.[8,9] Honeycomb beds may be mounted in either a horizontal or vertical position. Vertically oriented down-flow designs are usually used for coal-fired boilers with high-dust systems SCR applications to minimize fly ash deposition in the catalyst.[10]

Plates in the plate-type design are typically aligned vertically and the flue gas stream is downward.

In high-dust systems developed for boilers having high particulate matter concentrations, catalysts have large cells to facilitate particle movement through the cells. The ability of the catalyst to handle a flue gas stream with high levels of particulate matter is reflected by the *pitch*. Pitch is defined as the center-to-center distance between cells (honeycomb) or plates (plate-type).

The larger the pitch, the less surface contact with the flue gas. The catalyst should be designed to facilitate good contact with the gas stream and prevent plugging by particulate matter. Figure 11-7 displays a small-pitched and large-pitched honeycomb catalyst.

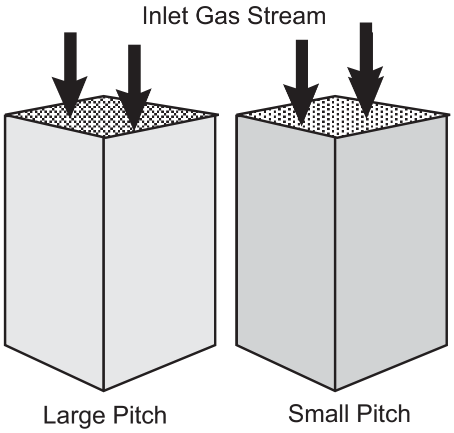


Figure 11-7. Large- and small-pitched honeycomb catalysts

Catalyst modules are stacked to fit the site-specific duct size. Gaskets are placed between catalyst modules to prevent gas seepage between modules.

Note: The broadcast video segment associated with this chapter includes a narrated video on an SCR system honeycomb catalyst unit illustrating the general characteristics of the unit. Classroom presentations of this course will also introduce this film segment.

11.5.3 Surface Reactions

NO_X reduction reactions occur on small sites on the surface of the catalyst or in the pore structure. Macropores and micropores in the catalyst provide increased surface area for better efficiency as shown in Figure 11-8.

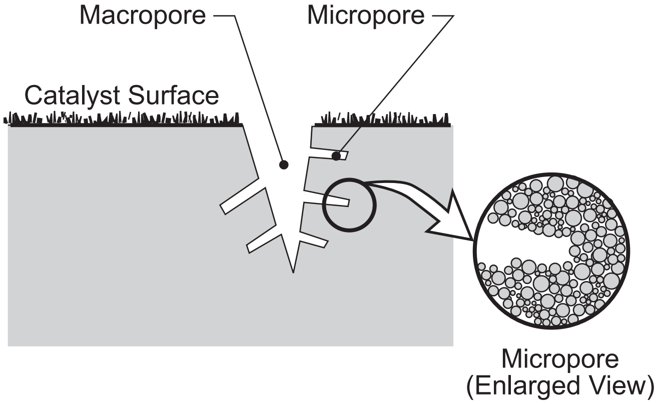
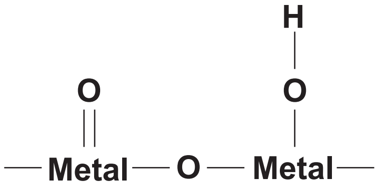


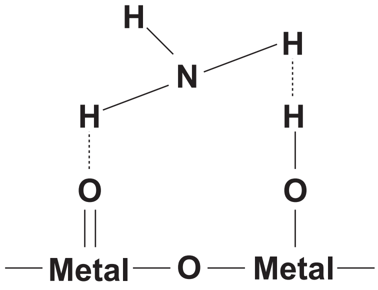
Figure 11-8. Catalyst surface and pore structure

Catalyst deactivation refers to chemical or physical blocking of the pore structures, resulting in less surface area available for the NO_X reduction reactions to occur.

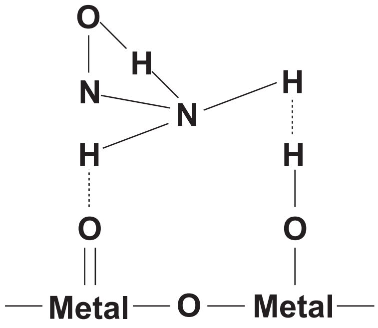
Active metal sites on a fresh catalyst contain a metal atom with a single or double bond to an oxygen molecule. Single bonded oxygen atoms are bonded either to two metal atoms or to a metal atom and a hydrogen atom.



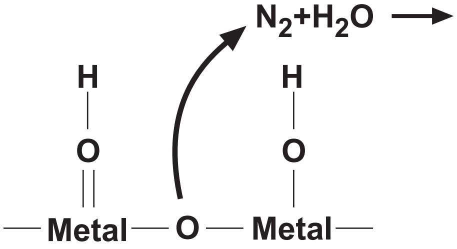
An open site provides an oxygen and a hydrogen atom available for adsorption of an NH_3 molecule.



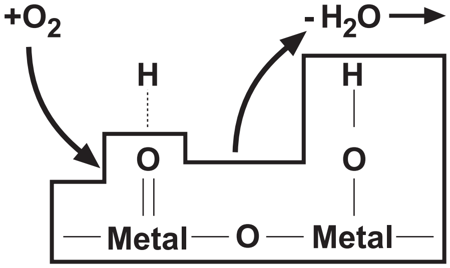
After the NH_3 molecule is bonded to the active catalyst site, the reaction with an NO molecule can occur. The N atom from the NO molecule and the N atom from the NH_3 molecule have become bonded during this step.



The two N bonded atoms are then released as N_2. Two H atoms from the ammonia molecule and the O atom from the nitric oxide molecule combine to form a water molecule, which is also released.



One H atom is left from the NO and NH_3 conversion to N_2 and H_2O. This H atom must be released to provide an open site. As discussed earlier, the flue gas must contain a minimal amount of O_2. The O_2 molecule attaches to a hydrogen molecule to form a water molecule, which is released.



This active site is now open for adsorption of another NH_3 molecule.

11.5.4 Deactivation and Deterioration

> Newly installed SCR systems are capable of reducing NO_X emissions by 80% to 90%. Over time, this efficiency is usually reduced slightly because of normal wear and aging of the catalyst bed and other SCR components.

NO_X reduction efficiency of the catalyst is impaired by physical or chemical damage to the catalyst. Such damage can result in significant loss of available reactant catalyst surface area, which undermines catalyst function. A discussion of some common problems follows.

Plugging is the physical blockage of channels or pores of the catalyst. Plugging is a result of heavy particulate matter loading (typically by fly ash), ammonium sulfate, or ammonium bisulfate. Loss of surface area directly affects the reduction of NO_X.

> Preventing plugged channels can be accomplished by properly sizing the pitch of the catalyst for the specific conditions.

Poisoning can irreversibly affect catalyst activity.[7] Poisoning results from the reaction of the catalyst with arsenic metals or alkaline metals such as sodium or potassium. Poison, such as phosphorus, lead, and arsenic (shown in Figure 11-9), permanently fixes itself to the active catalyst site creating a monolayer. The monolayer covers both the surface and pores of the catalyst on active and inactive sites.

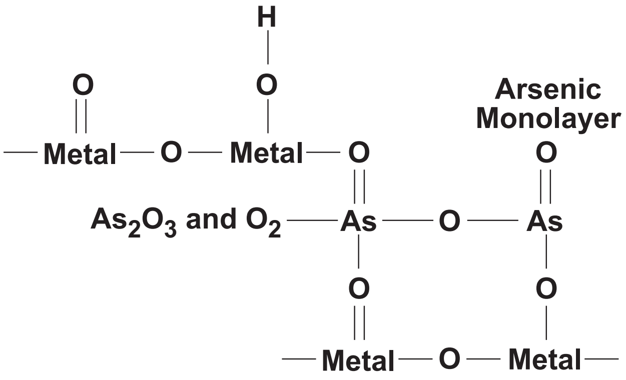


Figure 11-9. Arsenic poisoning of catalyst

Alkaline metals (e.g., Na, K) and earth metals (e.g., Ca, Mg) may poison the catalyst in a similar manner. Poisoning of an open site by alkaline metals is shown in Figure 11-10.

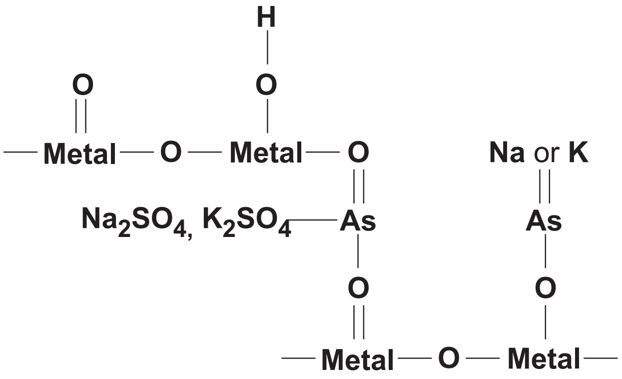


Figure 11-10. Alkaline metals poisoning of catalyst

Poisoning is costly because the catalyst is rendered useless and must be replaced. Poisoning is of greatest concern for coal-fired units because of inherent impurities in the fuel. Fuel additives can be used to reduce poisons released into the flue gas stream.

Masking occurs when the catalyst surface is coated with a foreign substance such as arsenic, calcium, or magnesium. The catalyst can be masked by particulate matter or chemicals adsorbing on the surface. A barrier is created between the active sites and the NO_X-laden flue gas.

Calcium sulfate is a common masking agent resulting from gaseous chemicals in the gas stream. SO_2 adheres to an active site along with calcium oxide to form a buildup of calcium sulfates that physically block access to the catalyst. Masking can be cleaned during the annual maintenance shutdown.

Blinding is the formation of an essentially impenetrable layer on the catalyst surface and is similar to masking. Blinding may result from (1) moisture condensation, (2) large concentrations of submicrometer particles, or (3) sticky particles deposited on the catalyst surface.

Plugging, masking and blinding are reversible situations. Installation of *soot blowers* will help reduce effects of these deactivation problems. Soot blowers periodically inject pressurized air or steam at the catalyst in order to discourage particulate matter build-up.

Sintering is the partial fusion of a material as a result of heating it above its melting point. At high gas temperatures, the catalyst bed can sinter and thereby reduce the accessibility of the catalyst to the nitrogen oxide-containing gas stream. Sintering begins to occur at around 800°F for vanadium/titanium catalysts. Sintering initially causes fusion of the micropores; as the temperature is increased macropores will also become fused.

Sintering can be avoided with proper location of the SCR system in the process. If necessary, specialized catalysts are available for elevated gas temperatures.

Erosion mainly occurs at the upstream exposed face of the bed. Mechanical erosion of the catalyst is a result of the abrasion of fly ash.

The effect of erosion can be reduced by hardening the edges of the catalyst exposed to the gas stream. The edges can also be tapered to reduce the abrasion effect.

As demonstrated in Figure 11-11, deactivation rates can be environmentally dependent. Exhaust gases that are high in particulate concentrations are likely to have higher catalyst deactivation rates than low dust streams.

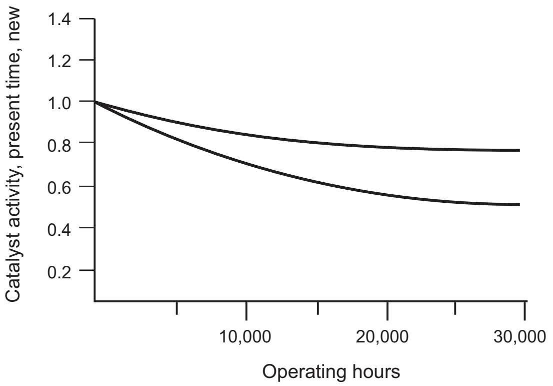


Figure 11-11. Catalyst deactivation

Catalyst Deterioration can be minimized in a number of ways. This includes developing new catalysts that have increased poison resistance either through the addition of materials to block the SO_2 conversion to SO_3 or through the development of new catalyst materials. Modification of the catalyst structure (e.g., edge hardening) can increase catalyst resistance to erosion. Size and distribution of the pore structure can be modified to minimize the poisoning reactions.

In addition, flue gas design and catalyst bed design can be optimized in an effort to minimize catalyst deterioration. Well-designed ammonia injection systems result in reduced ammonia slip emissions. Monitoring systems (see Section 11.6) are useful to provide operators with an indication of a problem and allow deterioration issues to be addressed early. Boiler operation is also critical to catalyst performance. For example, the boiler needs to be operated in the proper temperature range necessary for the SCR reactions to occur. Finally, in some cases fuel additives can be used to address arsenic poisoning.

11.5.5 Catalyst Management

Because the majority of the initial cost of an SCR system is associated with the catalyst, there is a strong incentive to optimize the performance of the catalyst. A catalyst management plan can successfully govern the schedule for catalyst replacement.

For example, the catalyst modules are often designed with sufficient space for three or more separate catalyst beds in series. Initially two beds can provide the necessary NO_X removal. As the catalyst deteriorates over time, the operator can install the third bed to maintain NO_X destruction efficiencies. Figure 11-12 displays a typical replacement cycle for a three-bed system.

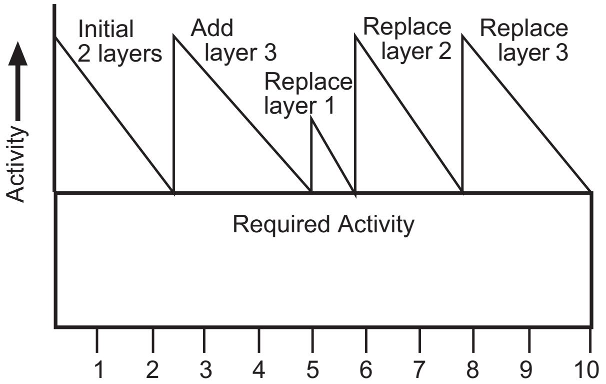


Figure 11-12. Catalyst replacement cycle

The schedule displayed in Figure 11-12 involves two fresh beds installed initially. The third bed is added in series after 2½ years. The fresh bed is always placed on the upstream side of the existing beds to provide optimal NO_X reduction. After another 2½ years have passed, one of the two original catalysts is removed and a fresh catalyst is inserted. The other original catalyst is replaced a year later. From this point on, the catalyst with the longest operating life is replaced by a fresh catalyst, which is inserted on the upstream side.

> The example rotation schedule guarantees that the operating life of each catalyst bed does not exceed six years. The actual operating life of the catalyst depends on a number of site-specific parameters, including the following:
>
> - SCR configuration (i.e., high dust, low dust, tail end)
> - Flue gas characteristics (e.g., trace elements, particulate matter)
> - Catalyst components
> - Catalyst composition (i.e., homogeneous, heterogeneous)
> - Physical catalyst characteristics (e.g., pitch, tapered face)
>
> The rotation schedule assumes proper operation and normal wear of the catalyst. The condition of the bed must be routinely inspected and monitored for deactivation or deterioration problems. Catalyst beds are equipped with a small removable section. The sample is removed and analyzed for determining the condition of the bed.

11.5.6 Design Considerations

SCR applications are customized to the requirements of each individual unit. One of the primary considerations is where to locate the SCR reactor bed. Other considerations are the amount of catalyst required to achieve the desired NO_X reductions and ammonia storage requirements.

The design of catalyst composition and pitch are affected by the following factors:

- Required level of NO_X reduction
- NO_X inlet concentrations
- Flue gas temperatures
- Allowable SO_2 conversion rates
- Allowable ammonia slip
- Particulate matter emission rate
- Particulate matter size distribution
- Fuel properties (e.g., fly ash and trace elements)
- Pressure drop
- Flue gas, NH_3, and NO_X distributions

- Catalyst life required
- Fly ash contamination
- Damage to downstream equipment

Space Velocity defines the size of a catalyst bed. To properly size the SCR catalyst volume, the following factors must be considered:

- NO reduction requirement
- SCR inlet NO concentrations
- Allowable NH_3 slip
- Catalyst bed static pressure drop

Space velocity is the amount of catalyst necessary to meet NO_X reduction goals, as defined in Equation 11-1.

$$\text{space velocity (1/hr)} = \frac{\text{flue gas flow rate (ft}^3\text{/hr)}}{\text{catalyst volume (ft}^3\text{)}} \qquad \text{Equation 11-1}$$

Necessary space velocity can be determined empirically, based on previous commercial installations or calculated theoretically by Equation 11-2.[1]

$$\text{k/SV} = -\ln\left(1 - \frac{x}{r}\right) + \frac{\ln\left(\frac{1-x}{1-x/r}\right)}{KN_o\,(1-r)} \qquad \text{Equation 11-2}$$

Where:

$$r = x + \frac{s}{N_o}$$

$$s = (r - x)\,N_o$$

k = rate constant
SV = space velocity
x = fractional conversion of NO_X
r = molar ratio of NH_3 to NO_X at reactor inlet
K = adsorption coefficient of NO_X on catalyst
N_O = NO_X concentration of the reactor inlet

If the catalyst space velocity is underestimated the system will not be able to meet the required NO_X emission reduction. In this case the catalyst volume is too small and the residence time of the flue gas passing through the bed will be inadequate.

Overestimation of the catalyst space velocity results in excess cost for unnecessary catalyst material and increased pressure drop across the system. A larger sized fan may be necessary to accommodate a higher static pressure drop.

11.5.7 Performance Considerations

Issues that affect performance of the SCR system are similar to those that are considered when designing the system. These include:

- Flue gas constituents
- Temperature of the flue gas needs to be in the range required for the catalyst to be effective.
- Distribution of the flue gas and ammonia prior to entering the reactor and the distribution of the velocity over the reactor bed.
- Operating conditions

Flue Gas Constituents
Contents of the flue gas can cause SCR system operation problems. Flue gas oxygen content is vital to SCR NO_X reduction reactions. Other crucial flue gas constituents are the inlet NO_X concentration, moisture, sulfur, and trace elements, such as arsenic, alkaline metals, and earth metals (Ca, Mg).

Figure 11-13 shows that 2% to 3% oxygen in the flue gas is required to maximize NO_X reduction in the gas stream. Although additional oxygen will have no measurable effect on NO_X reduction, the lack of sufficient oxygen will result in inefficient NO_X conversion.

> As shown in Reactions 11-1 and 11-2, oxygen is necessary for the conversion of NO_X to harmless molecular nitrogen (N_2) and water. Oxygen can become the limiting parameter for NO_X control efficiency when it falls below approximately 1.5% O_2 by volume. The flue gas at the SCR of most units contains substantially more than the minimum amount of oxygen because of normal excess air boiler firing rates and air infiltration upstream of the SCR system. Figure 11-11 displays the effect of oxygen on NO_X reduction for an SCR.

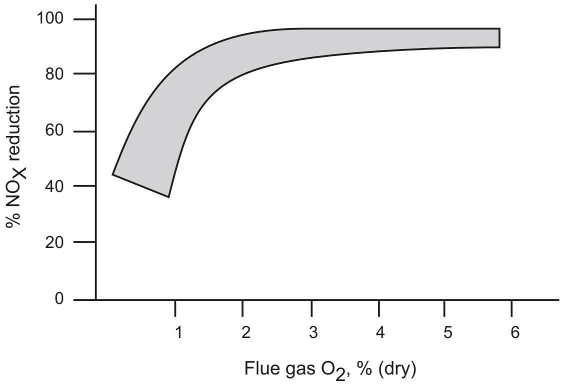


Figure 11-13. Relationship of flue gas oxygen and NO_x reduction

Figure 11-14 demonstrates that there is direct correlation between the concentration of NO_X in the inlet stream and the NO_X reduction achieved by the SCR system. In general, this correlation dictates that the greater the inlet NO_X levels (particularly at levels greater than 1 lb/MMBtu to 1.5 lb/MMBtu), the greater the NO_X reduction will be.

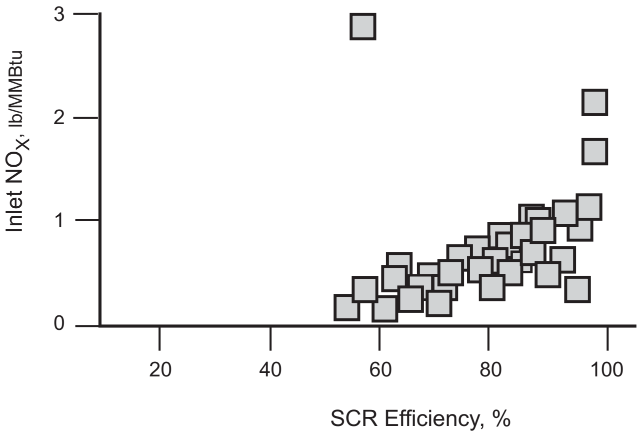


Figure 11-14. Effect of inlet NO_X concentration on SCR efficiency

Operating Conditions

The effect of thermal aging of the catalyst is demonstrated in Figure 11-15. The temperature range for optimal catalyst performance is between 550°F and 750°F (depending on the catalyst formulation). At temperatures above 750°F, sintering occurs and the performance of the catalyst is reduced.

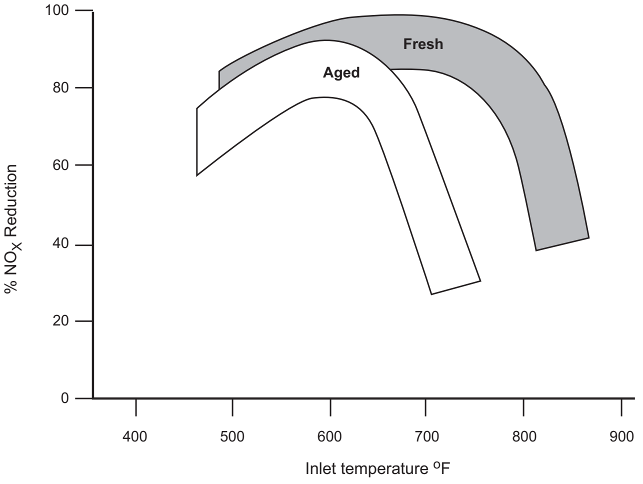


Figure 11-15. Effect of thermal aging of the catalyst

As shown in Figure 11-16, a stoichiometric ratio of one mole of ammonia to one mole of NO_X is the optimal ratio for maximizing NO_X reduction.

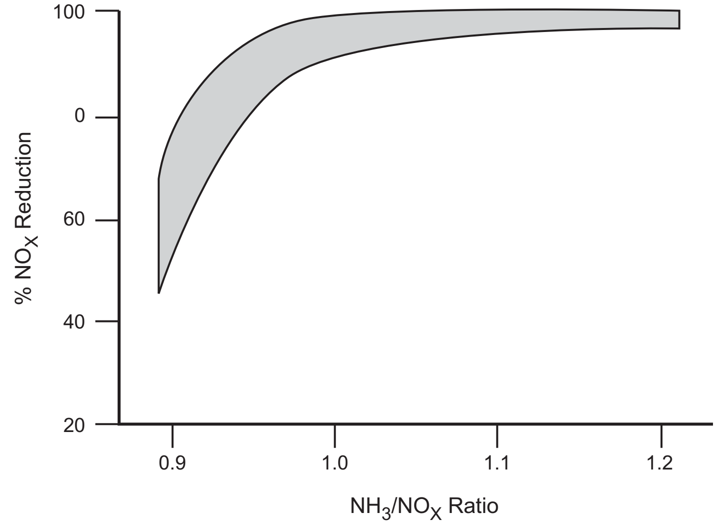


Figure 11-16. Effect of stoichiometric ratio on NO_X reduction

However, as previously mentioned, ammonia is typically injected at stoichiometric ratios of approximately 0.85:1.00 [3] to 0.90:1.00 [6] to maintain low ammonia slip levels.

Figure 11-17 demonstrates that the effect of the NH_3/NO_X stoichiometric ratio on ammonia slip emissions. NO_X concentrations in the flue gas and the stoichiometric ratio have significant impacts on ammonia slip.

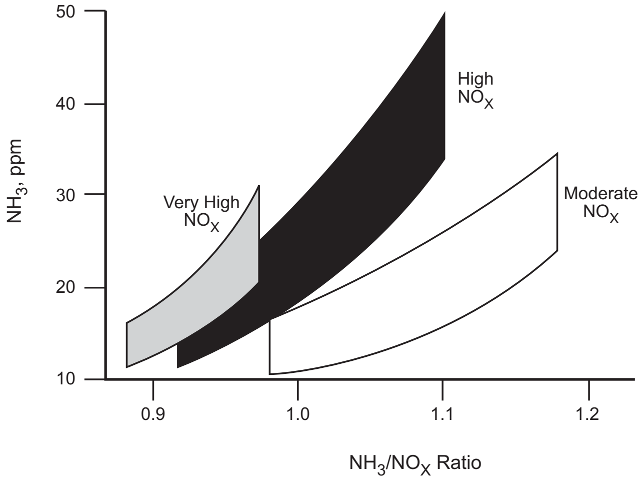


Figure 11-17. Effect of stoichiometric ratio on ammonia slip

Another factor that can influence the performance of the SCR is the operating status of the unit. Units that are continually operated at base load will achieve greater NO_X reductions than units that operate on a standby or intermittent basis. This difference is primarily the large temperature variations associated with startup and shutdown of the unit.

Fuel characteristics will also have a significant effect on the performance of the catalyst.

11.6 INSTRUMENTATION

Instrumentation used on an SCR system includes the following:

- Inlet gas temperatures
- Continuous emission monitoring (CEM) for outlet and possibly inlet NO_X
- CEM for outlet and possibly inlet O_2
- CEM for NH_3 slip
- Manometers for NH_3 injection rate and pressure drop across the catalyst
- Pressure gauges for monitoring NH_3
- Motor current for dilution fan

11.6.1 Temperature

As discussed earlier, the necessary temperature range for the SCR system depends on the type of catalyst. Most of the systems operate in the range of 550°F to 750°F (280°C to 400°C).[3] At temperatures exceeding approximately 670°F (350°C), the oxidation of ammonia begins to become significant and competes with Reactions 11-1 and 11-2.[8] At low temperatures, ammonium sulfate and bisulfate formation causes scaling and corrosion problems.

Gas temperature is an extremely important parameter to monitor. Inlet flue gas temperature to the catalyst bed is often used as the primary control signal to determine when to divert the gas stream to the bypass duct and stop reagent injection. Gas temperature can be used to determine when to send the gas stream to the SCR system during the startup of the combustion system. It can also be used to modulate reagent flow during boiler load variation.

The boiler steam flow meter can be used as a secondary indicator of the gas temperature. An advantage of this approach is that the steam rate gauge is not subject to monitoring problems caused by non-ideal conditions in the gas stream. Steam rate gauges provide a direct indication of changes in the boiler operating conditions. The main disadvantage of this approach is that the steam flow rate is not directly related to the gas temperature at the reagent injection location.

Accordingly, the general relationship between the steam flow rate and SCR system performance must be determined for the specific system.

11.6.2 NO_X Monitoring

This section provides a brief discussion of NO_X CEM for SCR systems. A detailed discussion of CEM can be found in Chapter 13.

In some systems, a NO_X continuous emission monitor upstream of the SCR bed controls the rate of ammonia feed. In other systems, the NO_X monitor is installed downstream of the catalyst bed.

NO_X CEMs provide a direct indication of the performance of the SCR system and can be used to simultaneously provide compliance data and SCR reagent feed system control data.

Sample lines for extractive-type CEM systems must be kept heated from the stack or breeching to the condenser. The condenser liquid bath temperature should be in the range of 35°F to 45°F (1.7°C to 7.2°C). Inadequate removal of water vapor can create the potential for analyzer damage. It can also affect the accuracy of the emission concentration measurement because the instrument is no longer receiving a “dry” sample gas. The presence of water vapor causes a lower-than-actual concentration value.

11.6.3 Oxygen Monitoring

Oxygen concentrations are measured at the stack along with the NO_X emission concentrations. Oxygen data are used primarily to adjust the measured NO_X concentration back to a standard oxygen level, usually 7% oxygen (dry basis). This provides a means to evaluate the compliance status of the facility without errors introduced by dilution of the stack gas stream.

Inlet oxygen concentration levels should be determined. CEM of the inlet may be necessary if the oxygen level should drop below 1.5%. Concentrations below this level may not provide sufficient O_2 for the catalyst reactions (Reactions 11-1 and 11-2).

It is important to note that normal oxygen concentration is a function of the combustion system operating rate. Oxygen concentration is at a minimum at full load and increases slightly as the load is decreased because of the need for higher excess air rates at low load.

In reviewing oxygen concentration data, it is also important to note that oxygen concentrations are often not spatially uniform at the measurement location. Problems caused by air infiltration or burner adjustment can create stratified gas streams with substantially different oxygen concentrations. Oxygen monitors sampling gas at only one or two locations in the duct or breeching may not accurately characterize the variations in oxygen concentration across the gas stream. Accordingly, the entire breeching or duct should be traversed with an oxygen monitor whenever there are concerns about oxygen concentration in the flue gas stream.

11.6.4 Ammonia Monitoring

Monitoring the ammonia slip is helpful to determine reagent injection rates, possible fly ash contamination, SCR inefficiency, and plume formation. However, continuous emission monitoring for NH_3 is presently unreliable. NH_3 is a soluble gas that can easily be “lost” during sampling. Careful attention should be made to insure that the CEM system is providing accurate and representative data.

11.6.5 Reagent Flow Rates and Pressures

The reagent supply system has a variety of liquid and gas stream pressure gauges and flow rate gauges. Usually, there are individual flow rate and pressure gauges on each injection nozzle. This is necessary to allow the operator the flexibility of adjusting each nozzle individually to optimize dispersion of the reagent into the gas stream.

11.6.6 Static Pressure Drop Across the Catalyst Bed

Plugging or blinding of the catalyst is indicated by a change in static pressure drop across the bed. Static pressure drop can also be used to determine soot-blowing intervals.

11.6.7 Fan Motor Current

Maintaining adequate dilution of the reagent stream is important for system performance and safety. The motor current of the dilution fan is an inexpensive and direct indication of the dilution air flow rate.

Ammonia slip increases once NH_3-to-air dilution ratios increase above the prescribed limit. The potential for explosion occurs if the dilution ratio increases above the NH_3 lower explosive limit (LEL) of approximately 15% .

If the motor current indicates that the air for dilution is higher than required, the reduction efficiency of NO_X is reduced.

Review Exercises

1. Why is NH_3 slip greater than 20 ppm undesirable?
   (Select all that apply.)
   a. Dramatically decreases the life of the catalyst.
   b. It may cause a secondary plume formation.
   c. It represents reagent loss.
   d. Fly ash contamination may occur.
   e. None of the above

2. Why is the tail end system the least popular SCR configuration?
   (Select all that apply.)
   a. Corrosion of downstream equipment (such as the APH and particulate control equipment) is possible.
   b. Plugging and masking of the catalyst is possible.
   c. Flue gas temperatures are higher than desired.
   d. Flue gas temperatures are lower than desired.
   e. None of the above

3. With proper operation, what is the control efficiency expected for SCR technology?
   a. 15% to 20%
   b. 25% to 50%
   c. 50% to 90%
   d. 93% to 98%

4. What is the concentration of NH_3 reagent injected upstream of the catalyst?
   a. 3 to 5 ppm
   b. 10 ppm
   c. 3% to 5%
   d. 10%
   e. None of the above

5. What compound(s) can be added to a catalyst to minimize SO_2 conversion?
   (Select all that apply.)
   a. Titanium dioxide
   b. Tungsten trioxide
   c. Vanadium pentoxide
   d. Zeolites
   e. None of the above

6. Which of the following catalyst problems can be reversed?
   (Select all that apply.)
   a. Erosion
   b. Plugging
   c. Blinding
   d. Poisoning
   e. Masking

   f. Sintering
   e. None of the above

7. During which of the following situations should flow be diverted from the SCR? (Select all that apply.)
   a. Startup
   b. Shutdown
   c. Periods of abnormally high flue gas temperatures
   d. Periods of abnormally high flue gas oxygen concentrations
   e. None of the above

8. With proper operation, what is the control efficiency expected for SCR technology with moderate to high inlet NO_X concentrations?
   a. 25% to 40%
   b. 45% to 65%
   c. 70% to 90%
   d. 93% to 98%

9. How much NH_3 reagent is required for an inlet flue gas stream containing 2.7 lb mole NO_X/hr?
   a. 2.4 lb moles NH_3/min
   b. 0.50 lb moles NH_3/min
   c. 0.45 lb moles NH_3/min
   d. 0.41 lb moles NH_3/min

References

---

[1] Clean Coal Technology. July 1997. *Control of Nitrogen Oxide Emissions: Selective Catalytic Reduction (SRC).* Topical Report Number 9.

[2] Tonn, D. P., and T. A. Uysal. March 18-20, 1998. *2200MW SCR Installation on New Coal-Fired Project.* Presented to the Institute of Clean Air Companies (ICAC) Forum '98. Durham, NC.

[3] Buschmann, J. C., and A. C. Larsson. March 18-20, 1998. Worldwide Experience with Selective Catalytic Reduction. Presented to the Institute of Clean Air Companies (ICAC) Forum '98. Durham, NC.

[4] Donnelly, J.R., and B. Brown. June 25-30, 1989. *JOY/Kawasaki Selective Catalytic Reduction De-*NO_X *Technology.* Presented at the 82nd Annual Meeting of the Air & Waste Management Association. Anaheim, CA.

[5] U.S. Environmental Protection Agency. March 1994. *Alternative Control Techniques Document –* NO_X *Emissions from Process Heaters* (Revised). EPA-453/R-93-034.

[6] Kokkinos, A., J.E. Cichanowicz, D. Eskinaze, J. Stallings, and G. Offen. November 1992. NO_X *Controls for Utility Boilers*. Highlights of the EPRI July 1992 Workshop. Air Waste Management Association, pp 1498-1505.

[7] U.S. Environmental Protection Agency. March 1994. *Alternative Control Techniques Document –* NO_X *Emissions from Cement Manufacturing.* EPA-453/R-94-004.

[8] U.S. Environmental Protection Agency. March 1994. *Alternative Control Techniques Document –* NO_X *Emissions from Glass Manufacturing.* EPA-453/R-94-037.

[9] Durilla, M., J. M. Chen, and B. K. Speronello. 1990. *Composite SCR Catalysts for* NO_X *Reduction.* Paper prepared by Engelhard, Inc.

[10] Sharreef, G.S., D.K. Stone, K.R. Ferry, K.L. Johnson, and K.S. Locke. June 21-26, 1992. *Selective Catalytic Reduction* NO_X *Control for Small Natural Gas-Fired Prime Movers.* Paper 92-136.06. Presented at the 85th Annual Meeting of the Air and Waste Management Association, Kansas City, MO.

12 Selective Non-Catalytic Reduction

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Identify the main industrial categories in which selective non-catalytic reduction (SNCR) has been applied.
2. Explain the operating principles of SNCR.
3. Identify the components associated with an SNCR system.
4. Identify the main considerations when designing and sizing an SNCR system.
5. Calculate the reagent feed rate based on the stoichiometry of the conversion reactions and the required outlet concentration.
6. Identify the parameters that are used to gauge the performance of an SNCR system.

12 Selective Non-Catalytic Reduction

Selective non-catalytic reduction (SNCR) systems were developed to supplement the nitrogen oxides control provided by combustion system modifications and low NO_X burners. SNCR systems use gas phase, homogeneous chemical reactions to chemically reduce a portion of the NO_X emissions to N_2 in a high temperature zone of the combustion system. SNCR systems are classified as an *add-on* technique because they eliminate a portion of the NO_X that is formed rather than simply suppressing the amount formed. They have been used effectively on a variety of industrial boilers, small utility boilers, and municipal waste incinerators. Their applications are gradually expanding to include use with gas reburning, SCR, and other NO_X control systems as part of combination and hybrid NO_X control systems.

12.1 DEVELOPMENT

SNCR systems were first developed in the early 1970s, soon after the enactment of the Clean Air Act Amendments of 1970. This development was encouraged, in part, by the NO_X control limits imposed on fossil fuel-fired boilers in the first New Source Performance Standards (NSPS) for utility and industrial boilers (40 CFR Part 60, Subpart D). The development of NO_X control techniques such as SNCR was also encouraged by the identification of NO_X as one of the main contributors to urban photochemical smog in Los Angeles.

The first commercial version of an SNCR system was provided by EXXON[1] and was called the EXXON Thermal De-NO_X® system. It was developed in 1971 and was first commercially applied in 1974.

Information concerning the Thermal De-NO_X® system was first published in several U.S. patents issued in the early 1970s.[1] Commercial applications were very limited at the time of development because most of the industrial control efforts focused on combustion modification techniques such as off-stoichiometric combustion, flue gas recirculation, and low NO_X burners. Furthermore, federal and state regulations promulgated in the mid- to late-1970s required NO_X reduction efficiencies that were within the reach of these combustion modification techniques.

In the mid-1970s and early 1980s, the Thermal De-NO_X ® system began to be commercially applied, especially on municipal waste incinerators and utility and industrial boilers in both Japan and Europe. These sources were under severe pressure to minimize emissions of all air pollutants, especially NO_X. Some gas and oil-fired industrial boilers in photochemically sensitive areas such as Los Angeles also began to apply SNCR technology to minimize NO_X emissions.

In the early 1980's, research sponsored in part by the Electric Power Research Institute (EPRI) resulted in the commercial application of a urea-based SNCR system. Prior to this time, all of the SNCR research and development had been concerned with systems that used ammonia as the feed material responsible for chemically reducing NO_X to N_2. The urea-based SNCR system was licensed to Fuel Tech and was provided commercially under the trade name NO_X OUT® in 1988.

With the advent of urea systems, two competing SNCR systems were available. Both of these systems have been benefiting from continuing design improvements based on field experience with existing applications. These improvements include an evolution in the types of components used in the system as well as in the basic operating system.

Applications

By the late 1980s SNCR systems were considered reasonably available control technology (RACT) for the control of NO_X emissions from industrial boilers and municipal waste incinerators. These continue to be their main areas of application because the design of SNCR systems is compatible with the combustion chambers for these sources.

Furthermore, some industrial boilers and municipal waste incinerators have emissions that are not well suited for other add-on control techniques, such as selective catalytic reduction.

It is anticipated that SNCR will be expanded to other sources such as utility boilers, metallurgical furnaces, glass melting furnaces and other types of process heaters.

Note: The broadcast video segment associated with this chapter includes a narrated video on a urea-based SNCR system that has been applied to a wood-fired spreader stoker boiler. Classroom presentation of this course will also introduce this film segment.

12.2 OPERATING PRINCIPLES

The basic operation of SNCR involves injecting a reagent above the active combustion chamber. The exact nature of the burner flame characteristics is not central to applying SNCR. As a result, SNCR is applicable to a variety of boiler types.

The types of reagents that can be used in SNCR systems include anhydrous ammonia, aqueous ammonia, and urea.

> As discussed in section 12.4.1, the urea can be mixed with aqueous methanol.

Regardless of the type of reagent, the operation involves storing, diluting and delivering the reagent to the gas stream.

> In ammonia-based SNCR systems, the ammonia gas or ammonia solution is injected into the post-combustion zone of the combustion system.

The chemical reaction that occurs is a gas-phase homogeneous reaction that occurs at fairly high temperatures. The ammonia reacts with NO and NO_2 to form molecular nitrogen and water vapor. No waste products are inherently generated by these reactions.

Temperature Dependence
Temperature is critical to ensuring that the SCNR will operate at its maximum efficiency. The reaction processes represented by Reactions 12-1, 12-2, and 12-3 are gas temperature dependent.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{Reaction 12-1}$$

$$4NH_3 + NO_2 \rightarrow N_2 \qquad \text{Reaction 12-2}$$

$$2NO + NH_2CONH_2 + 0.5O_2 \rightarrow 2N_2 + 2H_2O + CO_2 \qquad \text{Reaction 12-3}$$

Figure 12-1 shows the relationship of NO_X reduction to N_2 (i.e., NO_X reduction efficiency) as a function of the flue gas temperature. It should be noted that the NO_X reduction efficiency of the process can be negative for reasons that will be explained later in this chapter. It should also be noted that the broad ranges shown in Figure 12-1 depict the wide variation in SNCR performance from unit to unit. The peak conversion efficiency takes place at an approximate temperature range of 1,600°F to 1,900°F[2,3] (870°C to 1,040°C), as indicated in Figure 12-1.

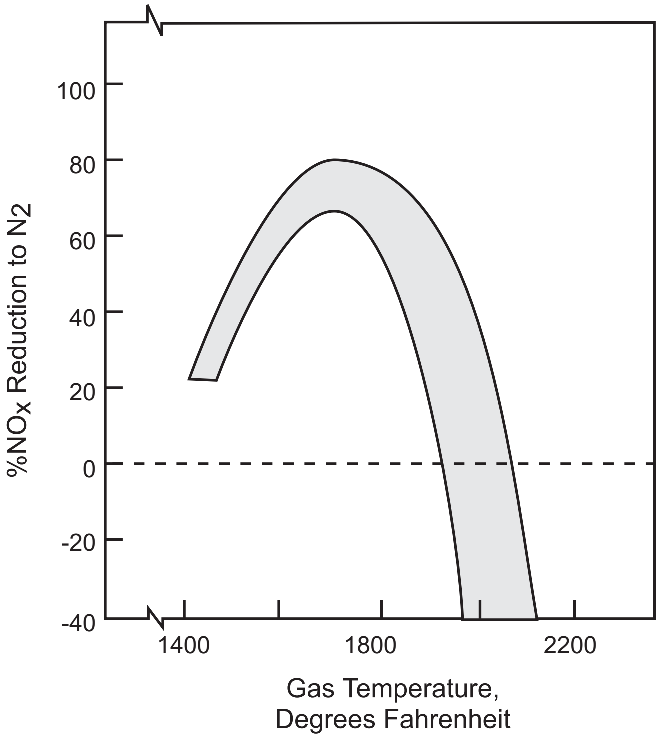


Figure 12-1. Gas temperature dependence of SNCR systems

The shape of the NO_X efficiency curve shown in Figure 12-2 is due to several competing reaction mechanisms for ammonia. Near the peak of the efficiency curve, Reactions 12-1 through 12-3 are dominant.

At temperatures above approximately 1,900°F (1,010°C), gas phase oxidation reactions between ammonia and oxygen are favored. As a result, most of the ammonia is lost (as shown in Reaction 12-4[1]) and is not available to react. For this reason, it is possible for an SNCR system operating at excessively high temperatures to create additional NO_X emissions and suffer negative control efficiencies.

$NH_3 + H_2O + 1.25\ O_2 \rightarrow NO + 2.5\ H_2O$ Reaction 12-4

At temperatures below 1,600°F (870°C), both the ammonia- and urea-based SNCR systems are vulnerable to ammonia emissions from the boiler.[2.] This is because the temperature is inadequate to initiate the gas phase reaction. NO_X generated in the boiler will pass through the system unaffected and the ammonia reagent will vaporize, mix with the gas stream, and be emitted as ammonia (called ammonia slip).

A temperature window of 1600°F to 1900°F is the ideal range for injecting the reagent and allowing adequate residence time for the reaction to go to completion. The impact on ammonia slip of operating below 1,600°F (870°C) is indicated in Figure 12-2. Ammonia concentrations greater than 20 ppm can be problematic because (1) ammonia can react with sulfuric acid to form sticky ammonium bisulfate and ammonium sulfate, and (2) ammonia can form a light-scattering particulate matter plume by reacting with chloride and/or sulfate compounds.

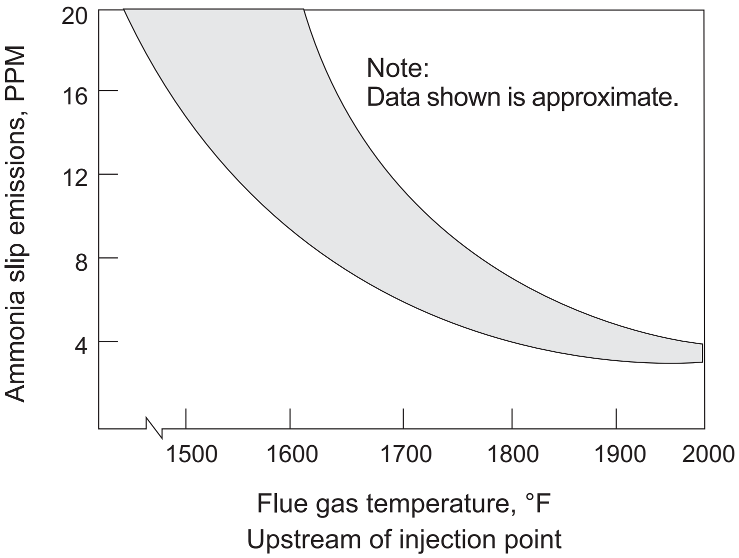


Figure 12-2. Ammonia slip emissions

Figures 12-3 and 12-4 demonstrate another temperature issue that must be considered when considering the use of SNCR with a specific application. These figures show the temperature profile of a cross-sectional view of a boiler at a point above the burner flames, but prior to the point of reagent injection. These figures demonstrate that the cross-sectional temperature profile spans a significant temperature range, and that the optimal temperature range for SNCR occurs in only a portion of the boiler. This can be caused by a number of factors, including burner configuration and air infiltration.

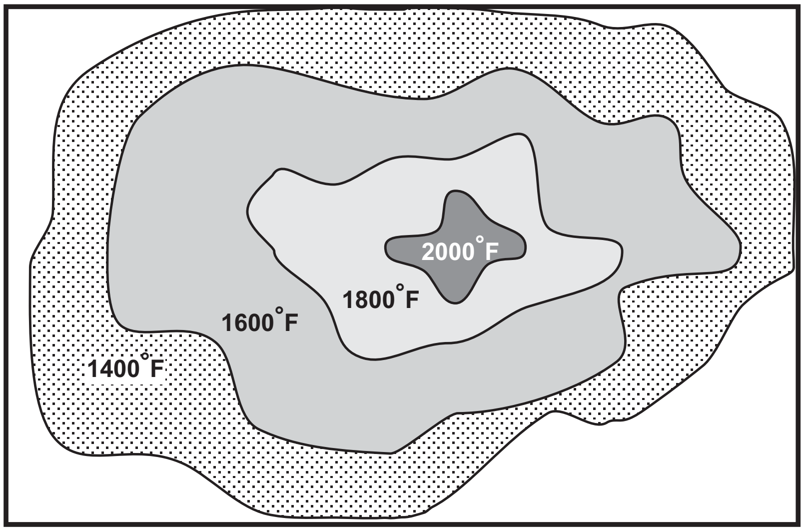


Figure 12-3. Boiler temperature profile (Cross-section above burner flames)

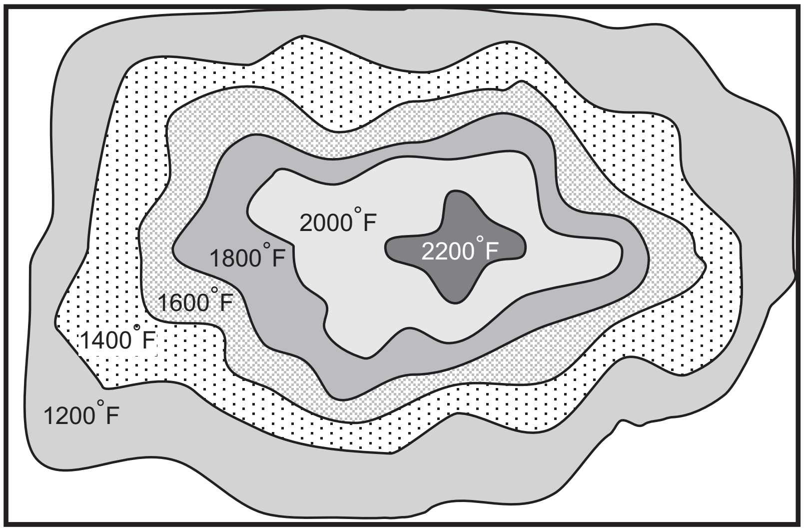
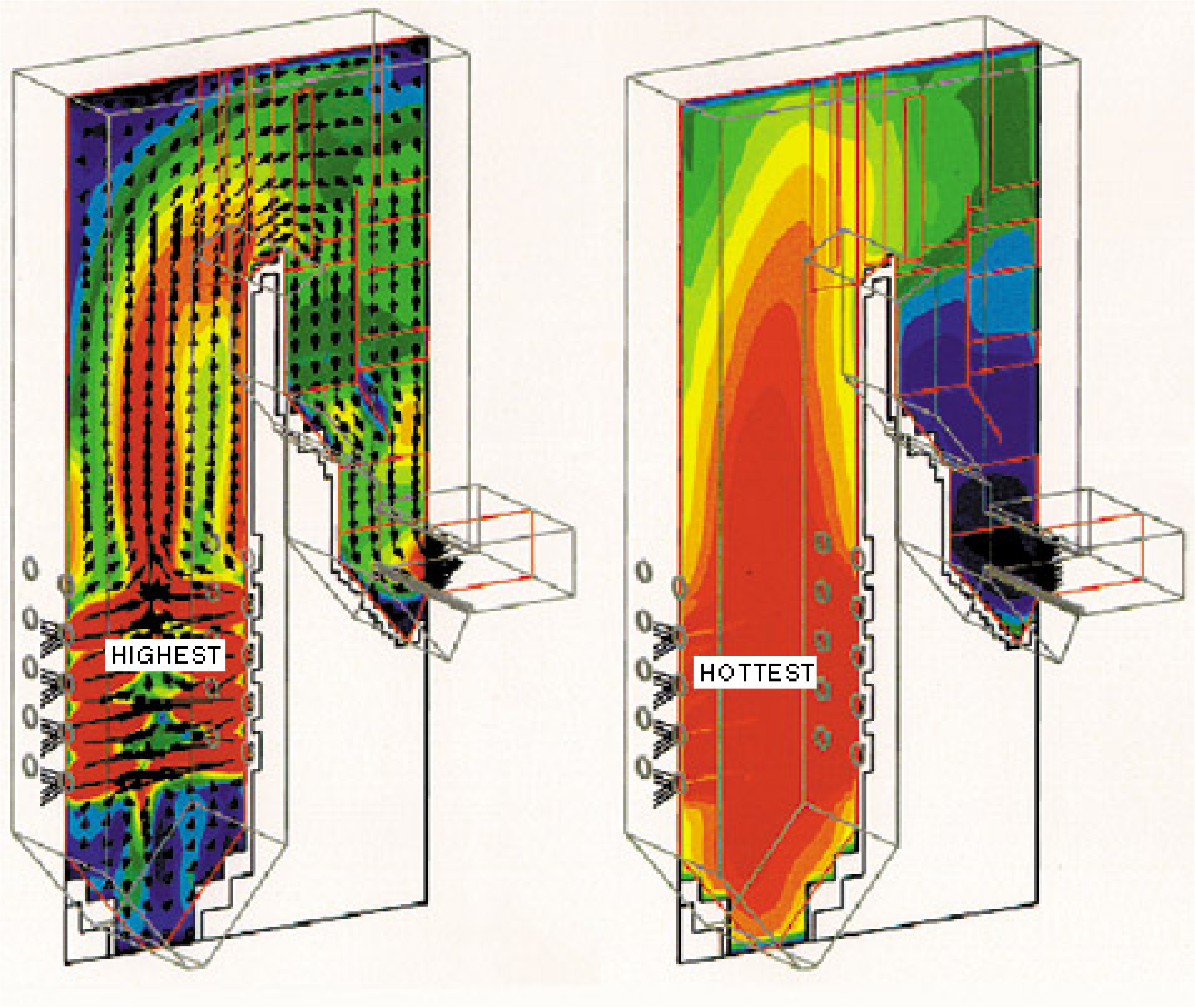


Figure 12-4. Boiler temperature profile (Cross-section above burner flames)

In addition to temperature variations, the amount of NO_X in different areas of the gas stream, as well as gas velocity stratification, can influence the application of SNCR to a particular boiler. Figure 12-5 is based on a Computational Fluid Dynamic (CFD) model, one of the two basic design approaches (further discussed in Section 12.4). This figure illustrates the concept of stratification.



Velocity Profile Temperature Profile

Figure 12-5. Temperature and gas flow rate profiles predicted by a CFD model
(Reprinted permission of Airflow Sciences, Inc., LaVonia, MI)

Solutions to the Temperature Dependence Problem

Locations of burners, over-fire air ports, and reagent injection nozzles can assist in creating an environment with a fairly uniform temperature profile more favorable to the use of SNCR.

> However, it is not always possible to locate a set of injection nozzles in the areas of the combustion system where this temperature range exists. For example, there are no accessible portions of a gas turbine or reciprocating engine for reagent injection. The combustion systems most adaptable to this add-on NO_X control technique are industrial boilers and municipal waste incinerators. In both of these types of sources, there is

an area within the refractory lined combustion chamber that is above the elevation of the burners and below the area of the heat exchange equipment. In these areas, the gas temperature range is compatible with the SNCR gas phase homogeneous reactions.

Several techniques have been developed to expand the temperature window for optimal performance of an SNCR system. These include the use of either methanol solution or hydrogen.[1] Methanol solution has the advantage because it is a highly soluble chemical that is injected in an aqueous form. The hydrogen gas must be stored under pressure and diluted in a carrier gas to a concentration well below its explosive range. The lower explosive limit for hydrogen is 2%; therefore, substantial dilution is needed. Supplemental hydrogen was used in some early systems installed in the late 1970s and early 1980s; however, hydrogen use has been largely abandoned in favor of SNCR design approaches that are well proven and less costly.

One variation of the SNCR process is the two-stage DeNO$_X$™ system that uses methanol with urea. A urea-methanol mixture is injected through the first set of nozzles while an aqueous methanol stream is injected in a downstream set of nozzles. A relatively high urea feed rate is used for this type of system. The methanol injection is used to control the ammonia slip. Methanol and other oxygenated compounds may extend the effective temperature range for NO$_X$ reduction down to 1,400°F (760°C); however, the use of this system is very limited because of the additional cost and complexity of using dual reagents.

Another difficulty in designing an SNCR system for a specific application is the ability to measure accurately the temperature profile in the boiler. Most testing equipment is not capable of withstanding the temperature conditions within the boiler. Water cooled probes are bulky but can be used to address this problem. In addition, radiant heat transfer from the burner flame to the probe can cause high readings. Similarly, temperature readings near the boiler walls can be influenced by transfer of heat from the probe to the cooler boiler walls, causing a low bias in the temperature reading. Because of the heat transfer conditions, the boiler interior is not an ideal environment for taking temperature readings. This creates an uncertainty about the accuracy of the temperature profile. Coupled with the small temperature window for optimal SNCR operation, there is then uncertainty about whether the SNCR will operate as designed. As a result, temperature data are supplemented with CFD and/or physical models to obtain a reliable temperature profile.

Typical NO$_X$ reduction efficiencies range from 20% to 60%[3] at the normal stoichiometric injection levels (ammonia and urea) and operating temperatures. Because of the non-uniformity of gas temperatures in any area of the combustion system, SNCR systems are often limited to overall NO$_X$ reduction efficiencies of less than 50%.

Reagent Evaporation

> For ammonia solutions, the first step involved in the process is the evaporation of the droplets to form ammonia gas. Droplet evaporation occurs in a fraction of a second when small droplets from the injection nozzles meet high gas temperatures.

The reagent must be delivered in a manner that allows adequate time for it to evaporate and react. Droplet evaporation rate is a function of gas temperature and droplet size. Droplet size is a function of the following:

- Nozzle operating pressure
- Nozzle orifice diameter
- Air pressure (for air assisted nozzles)
- Solution viscosity
- Solution surface tension

Some reagents have additives to produce reagent viscosity and surface tension that are ideal for droplet evaporation.

Stoichiometry

The stoichiometry of the overall reaction processes using ammonia as the reagent is shown in Reactions 12-5 and 12-6. The actual set of reactions responsible for the chemical reduction of NO is considerably more complicated than indicated by these summary reactions.

$4\ NH_3 + 4\ NO + O_2 \rightarrow 4\ N_2 + 6H_2O$	Reaction 12-5
$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$	Reaction 12-6

> Both of these reactions are gas-phase, homogeneous reactions, which means that the reactions occur entirely between gaseous compounds and no catalysts or particle surfaces are necessary. Only sufficient heat is needed to initiate the reactions. Oxygen is a necessary reactant to convert the hydrogen atoms in the ammonia to water vapor.
>
> Urea is stored and injected as an aqueous solution; therefore, these systems also have an initial droplet evaporation step. At high temperature, urea reacts to form ammonia radicals, NH_2. The NH_2 radicals then react with NO and NO_2 to form N_2.

The overall stoichiometry of the reaction using urea as the reagent is shown in Reaction 12-7.[4] The reaction products are the same as with ammonia, except carbon dioxide is also produced.

$2NO + NH_2CONH_2 + 0.5\ O_2 \rightarrow 2N_2 + 2\ H_2O + CO_2$	Reaction 12-7

The stoichiometry of Reactions 12-5, 12-6, and 12-7 are indicated by the relative number of molecules of ammonia or urea needed to react with the molecules of NO and NO_2. One of the important parameters describing the operation of an SNCR system is the actual ratio of ammonia or urea to the input level of NO_X. This is termed the *stoichiometric ratio* and is defined in Equation 12-1.

$$SR = \left[\frac{\text{moles of reagent supplied}}{\text{moles of } NO_X \text{ entering the system}} \right] \qquad \text{Equation 12-1}$$

It is possible to estimate the quantity of reagent needed for a given amount of NO_X.

Calculation of the quantity of reagent needed is discussed in detail in Section 12.4.3.

However, this is a site-specific calculation that varies with uncontrolled NO_X levels which are tied to boiler load and firing practices.

Another term that is related and often applied is the *utilization ratio*. As described in Equation 12-2, this is the ratio between the number of moles of NO_X reacted and the moles of reagent supplied.

$$UR = \left[\frac{\text{moles of } NO_X \text{ reacted}}{\text{moles of reagent entering the system}} \right] \qquad \text{Equation 12-2}$$

Figure 12-6 illustrates the relationship of NO_X reduction to stoichiometric ratios for both ammonia- and urea-based systems. The stoichiometric ratios of ammonia-based systems are often in the range of 0.8 to 1, indicating that the moles of ammonia supplied are 80% to 100% of the moles of NO_X formed in the boiler. The stoichiometric ratios of urea-based systems are often in the range of 0.4 to 0.5.

These values are lower than those for ammonia because, as indicated in Reaction 12-3, two moles of NO react with each mole of urea.

The use of reagent at the quantities dictated by the stoichiometric ratios results in NO_X reduction efficiencies in the range of 40% to 60%. Higher efficiencies can be obtained, however, there is a risk of increasing ammonia slip as the stoichiometric ratios are increased.

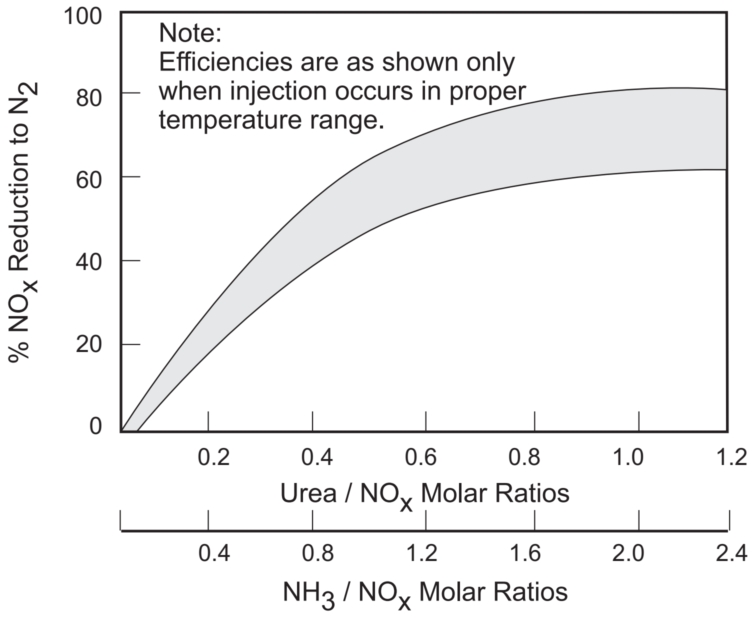


Figure 12-6. Relationship of NO_X reduction to stoichiometric ratios for ammonia- and urea-based systems

The utilization ratios of ammonia and urea systems are usually in the range of 20% to 50%.[5] This parameter takes into account the inefficiency inherent in reagent reactions. Even though there is almost enough reagent for complete NO_X reduction, the overall control efficiency is limited.

One approach to increasing NO_X reduction efficiencies is to use SNCR in combination with other post-combustion control technologies. For example, an SNCR system could operate at a higher stoichiometric ratio to achieve higher NO_X reduction efficiency. The ammonia slip generated by operating at the higher stoichiometric ratio could be addressed by installing a small SCR system downstream of the combustion zone and the heat exchangers to provide additional NO_X reductions and use the ammonia slip as part of the reagent for the SCR system. This arrangement is termed a *hybrid system*.

Problem 12-1. Stoichiometric Ratio

What is the stoichiometric ratio of an ammonia-based SNCR system operating with a gas flow rate of 100,000 SCFM, an inlet NO_X concentration of 350 ppm, an outlet NO_X concentration of 200 ppm, and an ammonia feed rate of 80 pounds per hour?

1. Moles of ammonia fed to the system

$$= \left[\frac{80 \text{ lb NH}_3}{\text{hr}}\right]\left[\frac{\text{lb moles NH}_3}{17 \text{ lb NH}_3}\right] = \left[\frac{4.7 \text{ lb moles NH}_3}{\text{hr}}\right]$$

2. Moles of NO_X (as NO) entering system

$$= \left[\frac{100{,}000 \text{ SCF}}{\text{min}}\right]\left[\frac{60 \text{ min}}{\text{hr}}\right]\left[\frac{\text{lb mole gas}}{385.3 \text{ SCF}}\right]\left[\frac{0.000350 \text{ lb moles NO}_X}{\text{lb mole gas}}\right]$$

$$= \left[\frac{5.45 \text{ lb moles NO}_X}{\text{hr}}\right]$$

3. Stoichiometric ratio

$$= \left[\frac{4.7 \text{ lb moles NH}_3\text{/hr.}}{5.45 \text{ lb moles NO}_X\text{/hr}}\right] = 0.86$$

Problem 12-2. Utilization Ratio

What is the utilization ratio of an ammonia-based SNCR system operating with a gas flow rate of 100,000 SCFM, an inlet NO_X concentration of 350 ppm, an outlet NO_X concentration of 200 ppm, and an ammonia feed rate of 30 pounds per hour?

1. Moles of ammonia fed to the system (as calculated in Problem 12-1).

$$= \left[\frac{4.7 \text{ lb moles NH}_3\text{/hr}}{5.45 \text{ lb moles NO}_x\text{/hr}}\right] = 0.86$$

2. Moles of NO_X (as NO) reacted

$$= \left[\frac{100{,}000 \text{ SCF}}{\text{min}}\right]\left[\frac{60 \text{ min}}{\text{hr}}\right]\left[\frac{\text{lb mole gas}}{385.3 \text{ SCF}}\right]\left[\frac{(0.000350 - 0.000200) \text{ lb moles NO}_X}{\text{lb mole gas}}\right]$$

$$= \left[\frac{2.34 \text{ lb moles NO}_X}{\text{hr}}\right]$$

3. Utilization Ratio

$$= \left[\frac{2.34 \text{ lb moles NO}_X\text{/hr}}{4.70 \text{ lb moles NO}_X\text{/hr}}\right] = 0.50$$

The utilization ratio is often expressed as a percent. For Problem 12-2, the utilization ratio of 0.50 is equivalent to a 50% value. This is on the high end of the normal range for SNCR utilization ratios.[3]

12.3 SYSTEM COMPONENTS

In contrast to the system components for an SCR system, the components associated with an SNCR system are not large or cumbersome. Components associated with an SNCR system include:

- Reagent storage and preparation
- Reagent injection nozzles
- NO_X emissions monitoring

12.3.1 Reagent Storage and Preparation

Reagents are stored in a concentrated form and diluted with a carrier gas or water.

When anhydrous ammonia is used, the ammonia gas must be mixed with air or steam to serve as a carrier gas stream. The presence of the carrier gas dilutes the ammonia below the explosive range and facilitates mixing in the flue gas stream because of the increased flue gas velocities and flow rates at the nozzles.

This ammonia-air mixture is injected at various points in the convection and superheater sections of the boiler. Multipoint ammonia injection grids are used to compensate for varying temperatures in the convection and superheater sections. Temperature differences result from changing boiler loads.

When aqueous solutions of ammonia or urea are used, the dilution water serves as the carrier stream. In these cases, it is important to achieve complete atomization of the droplets because the evaporation rate of the droplets is inversely related to droplet size. If the droplets evaporate too slowly, the ammonia could be released from the droplets in an area that is too cold for the NO_X reactions to proceed. The ammonia slip rate can be influenced significantly by the droplet size distribution. NO_X emissions from oil-, gas-, and coal-fired boilers and from waste incinerators can be reduced more than 20% to 60% by using ammonia or urea injection.

12.3.2 Injection Nozzles

The majority of SNCR systems have injection nozzles located at various elevations or locations within the boiler. This allows for optimal injection of reagent based on boiler operating conditions.

Three styles of injection nozzles are frequently used in SNCR systems. The most common type of injection nozzle is a multi-nozzle lance with compressed air-assisted atomization. The air pressures range from 40 to 80 psig in order to aid in the atomization of the liquid. Wall blowers use compressed air to dilute the reagent and to provide sufficient force to penetrate across the cross-flowing gas stream.[1,6] Nozzle design considerations are addressed in Section 12.4.2.

12.3.3 NO_X Emissions Monitoring

A continuous emissions monitor (CEM) for NO_X is a part of the system that adjusts the quantity of reagent delivered to the system. The amount of NO_X produced will vary over time and, consequently, the amount of reagent fed to the system must also vary. A CEM located in the exhaust gas vent relays data to the reagent delivery system that adjusts the rate of delivery to match the existing NO_X levels.

12.4 DESIGN AND SIZING

SNCR systems are usually applied to combustion systems that have already reduced their NO_X emission baselines by the application of combustion modifications and low NO_X burners. Reduction of the baseline emission rate minimizes the overall NO_X reduction necessary to achieve the regulatory limits and reduces reagent costs associated with an add-on SNCR system.

The following issues are the main considerations when designing and sizing an SNCR system:

- Type of reagent
- Location of reagent injection nozzles
- Types of reagent injection nozzles and blowers
- Control of reagent feed rates
- Performance monitoring instrumentation

12.4.1 Type of Reagent

There are four main reagent options for NO_X reduction.

1. Anhydrous ammonia
2. Aqueous ammonia
3. Aqueous urea
4. Aqueous urea and aqueous methanol

Anhydrous ammonia can be stored in pressurized storage vessels that have a capacity exceeding two weeks of normal SNCR system operation. The anhydrous ammonia must be diluted in a carrier gas stream such as air or nitrogen to ensure that the concentration remains well below 15%

by volume, the lower explosive limit for ammonia. The system includes an ammonia evaporator to convert the liquid ammonia into a gas that can be mixed with the carrier gas stream.

Typical ammonia concentrations at the point of injection into the combustion system are in the range of 1% to 3% by volume. Uniform Fire Codes, applicable in all parts of the country, make it necessary to include safeguards around the ammonia storage vessels to prevent fires during accidental release. Ammonia sensors and an emergency scrubber are often provided in the storage area to satisfy these fire prevention requirements.

Aqueous ammonia is shipped and stored in a concentrated form in standard storage vessels. The concentrated ammonia stream is diluted with water to generate the concentration appropriate for the SNCR system. This system does not require the fire protection safeguards required for anhydrous ammonia; however, the storage vessels are usually more costly than those for aqueous ammonia.

Aqueous urea and methanol are also shipped and stored in concentrated form. Urea is often at concentrations up to 50% by weight in water. Methanol concentrations are highly variable because of the various sources of methanol providing this material. These aqueous reagent solutions are diluted with water.

The dilution step allows the SNCR operator and designer another level of flexibility. By adjusting injector nozzle system, they can exert control over reagent solution flow rates and pressures at the point of injection and, accordingly, optimize the reagent dispersion into the combustion gas stream.

12.4.2 Injection Location and Nozzle Types

Reagent injection locations must have the appropriate gas temperature range when the combustion system is operating at mid- to high-loads. Under these combustion system operating conditions, gas temperatures are at their highest, and NO_X emissions are at a maximum. Because gas temperatures vary with combustion system load, it is generally necessary to have two separate levels of nozzles. In most cases, only one set will be operated at a time.

Gas temperature distribution must be reasonably uniform at the injection locations to ensure favorable conditions for the SNCR system. The gas temperature can be too cold for effective NO_X reduction along the outer walls of the combustion system, especially along the front wall of the boiler. Some gas temperatures in the center of the combustion system favor ammonia oxidation rather than NO_X reduction. If the SNCR system were applied in this system, the portion of the ammonia injected into the cold zone would form ammonia slip. The portion of the ammonia injected into the hot zone would be converted to additional NO_X.

This type of non-ideal temperature distribution is often caused by boiler firing problems. The infiltration of air from the charge chute of a municipal incinerator and/or air infiltration through cracked refractory of an incinerator or boiler can create a cold gas zone along the front wall of the combustion system.

Hot temperature zones can be caused by fuel maldistribution and/or the inherent firing conditions of the boiler or incinerator. For example, in a municipal incinerator, the first zone of the grate is used for fuel drying, and the second and third zones provide the most air to support combustion. The last one or two grate zones are used for ash burnout and cooling prior to movement of the ash into the ash pit. In this firing configuration, the most active area of combustion is the center of the incinerator.

A similar condition can be created in a spreader stoker boiler. Improper fuel size distributions and/or adjustment of one of more of the feeders can create a hot gas temperature zone in the center area of the boiler.

To the extent possible, gas temperature nonuniformity at the selected reagent injection location should be eliminated prior to the installation of the SNCR nozzles. This approach is preferred because temperature non-uniformity conditions are not constant. The locations and severity of hot and cold zones can shift frequently in response to changes in the fuels and operating conditions of the combustion system.

There are several ways to recognize temperature non-uniformity. In some cases, it is possible to map the gas temperature distribution using thermocouples attached to water cooled probes. These probes must be used with care because steam explosions can occur if there is a sudden loss of water flow to the probe. The use of the probes is often limited by the small size and limited number of ports into the combustion chamber. Nevertheless, temperature probes often provide a very useful indication of the extent of gas non-uniformity and the locations of cold and hot gas zones.

Computational fluid dynamic (CFD) models are often used to predict and correct gas flow non-uniformity conditions.[7, 8] CFD models were originally designed to model the gas flow conditions throughout a system; however, their use has expanded to provide predictive capability for the injection of fuel, the combustion of the fuel, and the transfer of heat from the flue gases. Accordingly, CFD combustion system models provide a complete computerized model of the system. When applied properly, they can provide temperature and gas flow rate profiles such as those shown previously in Figure 12-5.

A variety of CFD models are available, and they use different mathematical algorithms. Not all CFD models are appropriate for the specific combustion conditions of importance in SNCR system nozzle design. Furthermore, the accuracy of a CFD model can be compromised if it is necessary to make a number of assumptions concerning combustion conditions on the grates of a municipal waste incinerator or a spreader stoker boiler.

In preparing the CFD model of the reagent dispersion into the gas stream, it is important to consider that the reagent stream itself will modify the gas temperature profiles. The evaporation of aqueous solutions reduces the gas stream temperature. The rate of temperature reduction depends on the droplet size distribution of the injection nozzles. Small droplets can evaporate in fractions of a second, even in relatively cold portions of the combustion gas stream. Large droplets can penetrate relatively far into the gas stream and evaporate relatively slowly. The anticipated dilution ratio of the aqueous ammonia, urea, and methanol feed streams has an impact on the resulting gas temperature profiles at the point at which the reagents are in a gaseous form and are, therefore, available for the gas phase, homogeneous reactions with NO and NO_2.

The selection of an appropriate injection location and system design must also take into account the residence time for the necessary reactions. There must be sufficient residence time to allow for complete reaction between the NO and NO_2 and the reagents evaporated from aqueous solutions. If the gas stream immediately passes through a set of heat exchange tubes after reagent injection, the gas stream temperatures could drop below the levels necessary for efficient NO and NO_2 reduction.

Injection Nozzles

Proper distribution of the reagent(s) is very important for achieving the desired NO and NO_2 reduction efficiencies. The ammonia or urea reactant must be injected through a set of nozzles or wall blowers to achieve a distribution that is as uniform as possible.

Four general arrangements of injection nozzles are used.

1. Air-assisted high pressure single nozzle lances for aqueous solutions
2. Air-assisted high pressure multiple nozzle lances for aqueous solutions
3. High pressure nozzles for injection of anhydrous ammonia in a carrier gas
4. High pressure wall blowers for injection of anhydrous ammonia in a carrier gas.

Nozzles used for aqueous solutions of urea, ammonia, and methanol are conventional air-assisted high-pressure liquid nozzles. The compressed air pressures can usually be varied from levels as low as 40 psig to more than 80 psig to attain the necessary droplet size distribution. Liquid pressure to the nozzle can also be varied to adjust the overall reagent feed rate and to modify the droplet size distribution.

The flexibility provided by these types of nozzles provides the system designer with a number of options for optimizing reagent distribution. However, the complex array of variables that affect reagent distribution must also be considered by a system operator who is adjusting the reagent injection system to meet changing combustion system operating conditions. Variables that must be considered in optimizing an existing reagent injection system include the following:

- Air atomization pressure
- Reagent solution pressure
- Reagent density in the aqueous solution
- Nozzle orifice size and physical condition
- Orientation of the set of nozzles supplying reagent to a given injection location

It is difficult to make adjustments to a system when there are five highly interrelated influences. A number of separate trials are often needed to gradually identify the optimum system modifications necessary to adjust to changed combustion conditions. In some cases, the CFD models used in system design can be re-applied to help narrow the possible options for optimizing an existing system using air assisted nozzles for aqueous solutions.

A set of nozzles for anhydrous ammonia-carrier gas streams is slightly less complicated than for the air-assisted liquid nozzles. Primary design factors affecting the air stream include the following:

- Pressure of the reagent stream
- Flow rate of the reagent stream
- Nozzle orifice size
- Position of the nozzle in the combustion gas stream

Wall blowers are sometimes used in lieu of nozzles that project into the gas stream. Wall blowers use moderately high pressures and flow rates to ensure that the reagent is properly dispersed across the entire gas stream. The necessary blower discharge pressures and gas flow rates can be determined for a specific system using CFD models and/or cold flow models.

It is important to note that all of the nozzle designs must function properly when the boiler is at high load with high gas flow rates and temperatures, and when the boiler is at moderate load with reduced gas flow rates and temperatures. Accordingly, the goal of the designer and operator is not simply to identify a single optimum reagent injection operating condition, but to identify a necessary range of operating conditions that is adjusted to match boiler load conditions. This is a technically challenging requirement. Additionally, all injection nozzles and blowers require an opening for installation through the side wall or roof of the combustion system.

12.4.3 Control of Reagent Feed Rates

The reagent quantity requirement is the largest routine operating cost of an SNCR system, and is dependent on the following highly interrelated source-specific factors:

- Baseline NO_X levels and emission control requirements
- Gas temperature at the point of injection and droplet evaporation (aqueous systems)
- Effectiveness of reagent distribution
- Gas flow rate

The baseline NO_X levels and emission control requirements determine the overall total quantity of NO_X that must be chemically reduced. SNCR systems are usually installed after the completion of combustion modifications and/or low NO_X burners in order to reduce the range of baseline NO_X levels.

Gas temperature at the point of injection affects the urea utilization effectiveness. Injection on the cold side of the optimum temperature curve provides more effective utilization than operation on the hot side of the curve. (Refer to Figure 12-1.)

The effectiveness of reagent distribution is directly related to the total quantity of reagent necessary to achieve a regulatory NO_X emission limitation. The distribution effectiveness also strongly influences the vulnerability of the system to ammonia slip emissions.

The gas flow rate is important partially because it determines the total mass of NO_X that must be controlled in the system. Gas flow rate is also important because it affects the ability of a reagent injection system to achieve effective reagent distribution. Reagent distribution in large combustion systems is inherently more difficult than in small- to medium-sized combustion systems.

The reagent feed requirements of an SNCR system can be estimated based on the stoichiometry of the conversion reactions (refer to Reactions 12-5 through 12-7), the reagent utilization, the NO_X control requirements, and the size of the boiler. The calculations are illustrated in Problem 12-3.

Problem 12-3. Ammonia Feed Rate

Calculate the ammonia feed rate needed for a boiler having a gas flow rate of 75,000 SCFM, a baseline NO_X emission rate of 225 ppm, and a stack concentration of 125 ppm. Assume an ammonia utilization rate of 50%.

NO_X inlet

$$= \left[\frac{75000\text{ SCF}}{\text{min}}\right]\left[\frac{\text{lb mole total}}{385.3\text{SCF}}\right]\left[\frac{0.000225\text{ lb moles }NO_X}{\text{lb mole total}}\right] = \left[\frac{0.044\text{lb moles }NO_X}{\text{min}}\right]$$

NO_X outlet

$$= \left[\frac{75000\text{ SCF}}{\text{min}}\right]\left[\frac{\text{lb mole total}}{385.3\text{SCF}}\right]\left[\frac{0.000125\text{ lbs moles }NO_X}{\text{lb mole total}}\right] = \left[\frac{0.024\text{ lb moles }NO_X}{\text{min}}\right]$$

NO_X controlled = 0.044 lb moles NO_X/min - 0.024 lb moles NO_X/min

= 0.020 lb moles NO_X per minute

Reagent utilization = 50%

Reagent needed

$$= \left[\frac{100\%}{50\%\text{ utilization}}\right]\left[\frac{1\text{ lb mole }NH_3}{1\text{ lb mole }NO_x}\right]\left[\frac{0.020\text{ lb moles }NO_x}{\text{min}}\right]\left[\frac{17\text{ lb }NH_3}{\text{lb mole }NH_3}\right]$$

$$\text{Reagent needed} = \left[\frac{0.68\text{ lb }NH_3}{\text{min}}\right]$$

12.4.4 Performance Monitoring Instrumentation

A number of parameters are used to gauge the overall performance of the SNCR system.

12.4.4.1 NO_X Continuous Emission Monitoring

Nitrogen oxides CEMs provide a direct indication of the performance of the SNCR system and can be used to simultaneously provide compliance data and SNCR reagent feed system control data.

CEM data are often used as a trim signal for the reagent feed system that is controlled primarily by the furnace exit gas temperature (FEGT) and/or steam flow data. Chemiluminescence analyzers are the most common type of NO_X monitors presently used in CEM systems. Other major components of the CEM system include the sample acquisition and conditioning equipment, the calibration equipment, and the data acquisition system. The operating principles of NO_X CEMs are described in more detail in Chapter 13.

For extractive-type CEM systems, sample lines from the stack or breeching to the condenser must be kept heated. If the sample line has been cold for an extended time period, it is possible that corrosion, solids buildup, and/or pollutant absorption are occurring. It should be noted that extractive systems with dilution probes are not kept hot because the sample gas stream is diluted before condensation can occur.

Condenser liquid bath temperature should be in the range of 35°F to 45°F (1.7°C to 7.2°C). Inadequate removal of water vapor can create the potential for analyzer damage. It can also affect the accuracy of the emission concentration measurement because the instrument is no longer receiving a *dry* sample gas. The presence of water causes a lower-than-actual concentration value.

12.4.4.2 Ammonia Levels

Ammonia monitors can be used to detect ammonia slip. In addition to monitoring ammonia concentrations to determine ammonia slip levels, either opacity monitoring or Method 9 visible emissions readings can be used to detect ammonia slip problems. As previously discussed, ammonia slip can cause visible emissions because of the formation of ammonium salts.

12.4.4.3 Reagent Flow Rates and Pressures

The reagent (either ammonia or urea) supply system has a variety of liquid and gas stream pressure gauges and flow rate gauges. There can be a main flow monitor for the overall system, but it is more likely that there will be individual flow rate and pressure gauges on each injection nozzle. Individual instruments on each nozzle allows the operator flexibility to adjust each nozzle individually to optimize dispersion of the reagent into the gas stream. Dilution water feed rate monitors are located on each individual nozzle.

Nozzle operating conditions (including liquid pressure, compressed air pressures, and flow rates) can be monitored to give some indication of the performance of the unit. A substantial data base containing information gained from the operation of existing units is available to assist SNCR operators with optimizing the operation of their systems.

12.4.4.4 Furnace Exit Gas Temperature and Boiler Steam Rate

FEGT is often used as the primary control signal to the reagent feed system. It can be used to determine when reagent feed is started during the start-up of the combustion system. It can also be used to modulate reagent flow during boiler load variations. Due to extremely high temperatures in the combustion zone, thermocouples are rarely used in the FEGT unit. Shielded suction pyrometers, acoustical pyrometers, and optical pyrometers can often be used. The optical and acoustical pyrometers provide an indication of the gas temperature in the entire zone of the combustion gas stream scanned by the instrument.

In some cases, a boiler steam flow meter is used in lieu of the FEGT as the primary signal to the SNCR reagent feed system. One of the advantages of this approach is that the steam rate gauge is not subject to monitoring problems due to non-ideal conditions in the gas stream. Steam flow gauges are often accurate to plus or minus 5%. Furthermore, the steam rate gauges provide a direct indication of the changes in the boiler operating conditions. The main disadvantage of this approach is that the steam flow rate is not directly related to the gas temperature at the reagent injection location. Accordingly, the general relationship between the steam flow rate and the SNCR system performance must be determined for the specific system.

12.4.4.5 Oxygen Concentrations

Oxygen concentrations are measured at the stack, along with the NO_X emission concentrations. The oxygen data are used primarily to adjust the NO_X concentration measurements back to a standard oxygen level, usually 7% oxygen (dry basis). This provides a means to evaluate the compliance status of the facility without errors introduced by dilution of the stack gas stream.

In addition to its use in NO_X emission compliance measurements, oxygen data are also used to help evaluate the performance of the combustion system. Most combustion systems limit oxygen concentrations in order to avoid localized high concentrations in the peak temperature zones where thermal NO_X can form. Improperly adjusted fuel burners can have oxygen levels above the intended levels, resulting in high NO_X formation rates because of the availability of the oxygen in the peak temperature zones.

Air infiltration into the combustion system can also substantially increase oxygen levels. Air infiltration is due, in part, to the frequent thermal expansion and contraction of the combustion system during start-up, shut down, and operating rate changes. Oxygen entering with the infiltrating air can increase the thermal NO_X formation rates.

In reviewing oxygen concentration data, it is important to note that the normal oxygen concentrations are a function of the combustion system operating rate. Oxygen concentrations are at a minimum at full load and increase slightly as the load is decreased because of the need for higher excess air rates at low load. Accordingly, current oxygen concentration data should be compared against baseline data for the same combustion system operating rate (load).

In reviewing the oxygen concentration data, it is also important to note that the oxygen concentrations are often not spatially uniform at the measurement location. Problems caused by air infiltration or burner adjustment can create stratified gas streams with substantial differences in oxygen concentrations. Oxygen monitors sampling gas at only one or two locations in the duct or breeching may not accurately characterize the variations in oxygen concentration across the gas stream. Accordingly, the entire breeching or duct should be traversed with an oxygen monitor whenever there are concerns about oxygen concentrations in the flue gas stream.

12.5 OPERATION

12.5.1 Secondary Pollutants

SNCR systems, like many other air pollution control devices, effectively control one air pollutant while creating limited quantities of other air pollutants. The additional air pollutants result from undesirable chemical reactions and are termed *secondary air pollutants*.

The most prominent secondary pollutant in SNCR systems is ammonia slip. Ammonia can react with residual sulfuric acid vapor to generate very sticky ammonium sulfate and ammonium bisulfate.[1] These compounds can foul downstream heat exchange equipment, especially the air preheaters.

Ammonia can also react with hydrogen chloride in the gas stream to form a highly visible ammonia chloride detached plume.[1] The levels of ammonia chloride believed necessary to create this plume are in the general range of 20 ppm to 40 ppm, well above the levels typically present in an SNCR system. This *plume threshold* concentration is highly dependent on the concentration of hydrogen chloride and the ambient temperature. Ammonia chloride forms most readily when the ambient temperature is low.

Ammonia is not listed as a toxic air pollutant on the CAAA Title III list of hazardous air pollutants. It is, however, a Superfund Amendments and Reauthorization Act (SARA) Title II hazardous material, and some regulatory agencies have taken the position that ammonia is toxic and have specified emission regulations.

Under some operating conditions, SNCR systems can generate N_2O,[2] which is classified as a greenhouse gas. The limited data available concerning N_2O suggest that SNCR systems using urea are more vulnerable to this secondary pollutant. However, it is important to note that N_2O formation is rarely measured in full-scale systems, and there are insufficient data presently available to determine if N_2O levels from any SNCR systems are of concern.

Increased carbon monoxide emission concentrations have been observed during tests on some SNCR systems. There are no clear chemical mechanisms directly relating SNCR system operation and carbon monoxide formation. It is possible that this increase is due to normal variability of combustion modifications and low NO_X burners that are generally used in combination with SNCR systems.

In municipal incinerator applications, concerns have been expressed about the interference of SNCR systems with mercury collection. By modifying the partitioning of mercury between its elemental and compound forms, it is possible that an SNCR system could reduce the quantity of mercury adsorbed on the surfaces of carbonaceous particulate matter. However, there are little data applicable to full-scale systems to evaluate the significance of any relationships between SNCR system operation and mercury control effectiveness.

12.5.2 Startup and Shutdown

SNCR systems are usually not operated during startup and shutdown conditions. During both of these operating conditions, the gas temperature profiles at the reagent injection locations are too cold to permit proper operation. Injection of reagent under these conditions could lead to severe ammonia slip emissions. NO_X concentrations during startup and shutdown are also very low due, in part, to the cold operating temperatures in the combustion system.

SNCR systems designed to control NO_X during the ozone season can easily be turned off during the off-season. This can substantially reduce reagent costs.

12.5.3 Ash Quality

Both ammonia- and urea-based SNCR systems are vulnerable to the adsorption of ammonia on particulate matter collected in electrostatic precipitators and fabric filters. The ammonia substantially reduces the quality of the ash and often makes it unfit for sale. Consequently, it must be discarded to landfills. This doubly impacts the overall cost of operation by adding the landfill disposal costs and by eliminating the revenue generated by fly ash sales.

12.5.4 Maintenance

The reagent injection nozzles and/or blowers are the main components requiring frequent maintenance. Injection nozzles that protrude into the combustion furnace are vulnerable to the accumulation of ash and/or slag. Thermal damage can occur if the nozzles do not withdraw automatically upon the failure of reagent liquid flow.

Injection nozzles must be inspected on a routine basis to confirm if any of the nozzle orifices are worn or partially plugged. Problems with the nozzle orifices affect the size distribution of the sprays and thereby affect the adequacy of reagent distribution into the combustion gas stream.

Combustion system maintenance is very important to the proper operation of an SNCR system. Changes in fuel sizing, fuel-grate distribution (stoker boilers), burner operation (gas-, oil-, and pulverized coal-fired boilers), and overfire air settings (all boilers and incinerators) can affect the gas temperature distribution at the reagent nozzle locations. These combustion system changes can also affect the baseline NO_X concentrations.

Review Exercises

1. What is the optimum gas temperature range for SNCR gas phase, homogeneous NO_X reduction reactions?
    a. 1200°F to 1600°F
    b. 1600°F to 1900°F
    c. 1900°F to 2200°F
    d. 2200°F to 2500°F

2. What is the stochiometric relationship required to react ammonia with one mole of NO in a combustion gas stream?
    a. One mole of NH_3 per mole of NO_X
    b. Two moles of NH_3 per mole of NO_X
    c. One-half mole of NH_3 per mole of NO_X
    d. None of the above

3. What is the stochiometric relationship required to react urea with one mole of NO in a combustion gas stream?
    a. One mole of urea per mole of NO_X
    b. Two moles of urea per mole of NO_X
    c. One-half mole of urea per mole of NO_X
    d. None of the above

4. What is the equivalence ratio?
    a. Moles of reagent injected per moles of NO_X reduced
    b. Moles of NO_X reduced per mole of reagent injected
    c. Pounds of reagent injected per pound of NO_X reduced
    d. Pounds of NO_X reduced per mole of reagent injected

5. What conditions maximize the equivalence ratio?
    a. Gas temperatures on the low end of the optimum temperature range
    b. Gas temperatures on the high end of the optimum temperature range
    c. Gas temperatures below 1200°F
    d. Gas temperatures higher than 2500°F

6. What factors affect the quantity of reagent needed?
    a. Gas flow rate
    b. Equivalence ratio
    c. NO_X baseline levels and control requirements
    d. All of the above

7. What are the main instruments often used to control reagent feed during boiler load changes and other operational changes in the combustion system?
   a. Furnace exit gas temperature
   b. Steam flow rate
   c. NO_X CEM
   d. All of the above

8. What factors affect the distribution of an aqueous reagent injected through air-assisted nozzles?
   a. Compressed air pressure
   b. Liquid pressure
   c. Nozzle orifice diameter
   d. Liquid flow rate
   e. All of the above

9. What secondary pollutants might form as result of operating an SNCR system? (Select all that apply.)
   a. Sulfuric acid
   b. Ammonium chloride
   c. Mercury
   d. Nitrous oxide
   e. Carbon monoxide
   f. Hydrogen chloride
   g. Formaldehyde
   h. None of the above

10. Why are SNCR systems often used in combination with combustion system modifications and low NO_X burners?
   a. Reagent costs are reduced by the decreased NO_X levels provided by combustion modifications and low NO_X burners.
   b. Combustion modifications and low NO_X burners can generate organic compounds and carbon monoxide that enhance the SNCR reactions.
   c. Combustion modifications and low NO_X burners affect the gas temperature distribution in the gas stream.
   d. None of the above.

References

---

[1] Hurst, B. E and C.M. White. June 1986. *Thermal De-*$NO_X^{®}$*: A Commercial Selective Noncatalytic* NO_X *Reduction Process for Waste-to-Energy Applications.* Paper presented at the Municipal Waste Incinerator Conference. Pages 119-127.

[2] Jones, D.G. et al. June 24-29, 1990. *Urea Injection* NO_X *Removal in European Coal-Fired Boilers and MSW Incinerator Plants*. Presented at the 83rd Annual Meeting and Exhibition of the Air and Waste Management Association. Pittsburgh, PA.

[3] Makansi, J. May 1993. *Special Report, Reducing* NO_X *Emissions from Power Plants.* Power, pp 11-28.

[4] Fuel Tech. Unpublished notes dated April 1989. *The* NO_X*OUT® Process: Technology and Commercial Overview.*

[5] Straudt, J.F. et. al. March 18-20, 1998. *Optimizing Selective Non-Catalytic Reduction Systems for Cost-Effective Operation on Coal-Fired Electric Utility Boilers*. Paper presented at the ICAC Forum 98. Durham, NC.

[6] Exxon. July 1987. *Improved ER&E Thermal De*NO_X *Process.*

[7] Comparato, J.R., J.M. Boyle, and W.F. Michaels. March 18-20, 1998. Nalco Fuel Tech. *CFD Modeling of Urea-Based SNCR and Hybrid Performance of Large Utility Boilers.* Paper presented at the ICAC Forum 98. Durham, NC.

[8] Urbas and J. Boyle. March 18-20, 1998. *Design and Optimization of SNCR/SCR Hybrid on a Group 1 Boiler in the Ozone Transport Region.* Paper presented at the ICAC Forum 98. Durham, NC.

13 Continuous Emission Monitoring

STUDENT OBJECTIVES

When you have mastered the material in this chapter, you should be able to do the following:

1. Explain the regulatory drivers that can require the installation of CEM systems.
2. Explain the various measurement techniques that can be used in CEM systems.
3. Identify the different types of CEM systems.
4. Describe the different types of extractive and in-situ CEM systems.
5. Explain the concept of parameter monitoring and identify the different types of parameter monitoring.
6. Identify the performance specifications that are used to ensure the CEM system is collecting data that meets the intended purpose.
7. Describe the Relative Accuracy Test Audit and explain how to calculate the relative accuracy.
8. Identify the common types of oxygen analyzers.
9. Calculate the NO_X concentration on a wet and dry basis.

13 Continuous Emission Monitoring

Continuous emission monitoring (CEM) provides real-time immediate indication of emissions. As discussed in earlier chapters, NO and NO_2 are formed simultaneously in combustion processes and other high temperature operations. NO typically represents 90% to 95% of NO_X for these emission sources. NO is insoluble while NO_2 is moderately soluble. Moisture in the flue gas can be removed with only a slight loss of NO_X because NO_2 represents a minor portion of the total NO_X in a sampled stream. The ability to remove moisture from the sample gas prior to measurement opens many CEM system configuration options.

NO_X is determined with an assortment of measurement techniques. NO absorbs light in portions of the ultraviolet (UV), visible, and infrared (IR) spectra bands. These absorbent bands allow for a variety of spectroscopy measurement techniques. Another measurement technique is based on the principle of chemiluminescence resulting from NO and ozone interaction.

Continuous monitoring techniques are also used for measuring ammonia. These systems are relatively similar to those for measuring NO_X, except that some newer techniques have recently developed for ammonia.

Typical CEM systems are comprised of analyzers, a data acquisition system, a sample acquisition and conditioning system, and calibration equipment. They typically include a system for injecting calibration gases for daily calibration and quarterly audits.

13.1 CEM REGULATORY PROGRAM

Regulations and monitoring are interrelated. Regulatory requirements dictate the types of CEM systems that are to be installed and the manner in which they are to be operated. Alternatively, the advancement and development of monitoring technologies can result in regulations specifying the use of such technologies.

CEM regulatory programs have three distinct phases. The first is the *implementation*. This includes the regulations that require certain source categories to install CEM systems. The next phase is *certification* where the source must demonstrate that the CEM system operates in a concise and accurate manner. EPA, the International Standards Organization (ISO) and the American Society for Testing Materials (ASTM) have standards for conducting such certifications. Finally, after the CEM system is installed and certified, it must operate for long periods of time. The typical lifetime of a CEM system can be five to ten years, depending on the type of system and how well it is maintained. If a quality assurance plan is implemented, the CEM system can provide data availability for 95% to 99% of the time.

13.1.1 Implementing Rules

The regulations or rules that require the installation and use of CEM systems can be either federal or state/local. The first programs to be established were the Federal New Source Performance Standards (NSPS) that are codified in 40 CFR Part 60. However, state and local agencies can also require CEMs through their permit programs.

Through the NSPS program, EPA requires permanently installed CEM systems for NO_X monitoring at fossil fuel-fired steam generators, electric utilities, industrial and commercial steam generating units, municipal waste combustion, and nitric acid plants. More recently, the acid rain program in 40 CFR Parts 75 and 76 has required that NO_X be continuously monitored as part of the emissions trading program.

State/local air agencies are mandated by various federal programs to require sources to install (or allow as an option to install) a CEM system. Some examples include the Prevention of Significant Deterioration (PSD) and the Compliance Assurance Monitoring (CAM) programs. Another state/local program that requires NO_X monitoring is the RECLAIM program in California, which is similar to the Acid Rain Program, but on a regional level instead of a national level.

Other discretionary programs such variances, orders and court-ordered agreements can require the installation of a CEM system.

Note: The next section on Measurement Techniques does not appear in the broadcast video until after the discussion of extractive CEM systems.

13.2 MEASUREMENT TECHNIQUES

13.2.1 NO_X Measurement Techniques

Many commercial CEM NO_X analyzers, based on a variety of measurement techniques, are available.

$$Tr = \frac{I}{I_o} = e^{\alpha(\lambda)cl} \qquad \text{Equation 13-1}$$

Where:
Tr = transmittance of light through the flue gas
I_o = intensity of the light entering the gas per unit time
I = intensity of the light leaving the flue gas per unit time
$\alpha(\lambda)$ = molecular absorption coefficient
c = pollutant concentration
l = path length of light

Methods of NO_X measurement are chemiluminescence, infrared spectroscopy, ultraviolet spectroscopy, and electrochemical cells.

The common types of monitors presently used for nitrogen oxides determination with *extractive* systems use the following techniques:

- Chemiluminescence (NO_X)
- NDIR spectroscopy (NO)
- Gas filter correlation spectroscopy (NO)
- Nondispersive ultraviolet spectroscopy (NO_X)
- Polarography (NO_X)

In-situ monitors use the following methods:

- Gas filter correlation spectroscopy (NO)
- Differential absorption spectroscopy (NO)
  - ◊ Using diffraction grating
  - ◊ Using diode array detectors
- Diode array detectors (NO)
- Polarography (NO).

Extractive and in-situ CEM systems are discussed later in this chaper.

13.2.1.1 Chemiluminescence

Chemiluminescence analyzers are the most common type of NO_X emission monitors presently applied to CEM systems.

The principle of chemiluminescence involves the reaction of NO and instrument-generated ozone as shown in Figure 13-1.

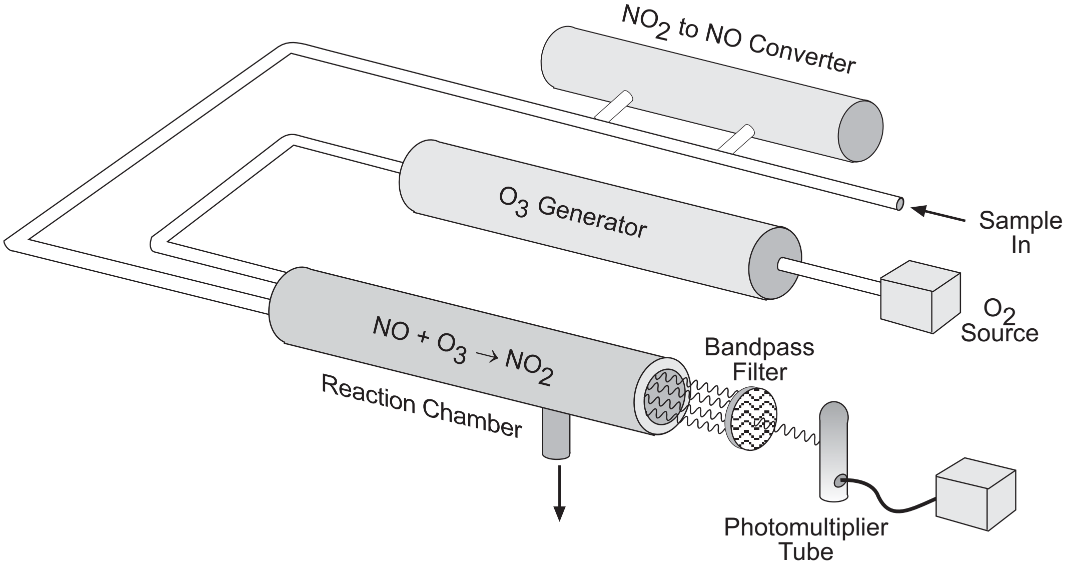


Figure 13-1. Chemiluminescent methodology

Before analysis, sampled gas is directed through a thermal converter to reduce any NO_2 to NO. The gas sample is then blended with instrument-generated ozone in a reaction chamber where the NO is converted to electronically excited NO_2 molecules, as shown in Reaction 13-1.

$NO + O_3 \rightarrow NO_2^* + O_2$	Reaction 13-1

The excited NO_2 molecules quickly release their excess energy by emitting a photon as they drop to a lower energy level (Reaction 13-2). The photons, or light emissions, are directly proportion to the NO concentration in the sampled gas. The light emissions for a narrow wavelength corresponding to the reaction are monitored by a photomultiplier tube.

$NO_2 \rightarrow NO_2 + hv$	Reaction 13-2

Ammonia can also be measured with this technique by first converting the ammonia to NO in a converter and then measuring the NO in the analyzer.

13.2.1.2 Spectroscopic Techniques

Since NO_X absorbs both IR and UV light, spectroscopic techniques can use either region of the spectrum. These techniques include: differential absorption spectroscopy; gas filter correlation spectroscopy; Fourier transform infrared (FTIR) spectroscopy; and second derivative spectroscopy. Of these four methods, all but FTIR spectroscopy can be used in either extractive or in-situ systems. FTIR spectroscopy can only be used in extractive systems.

Differential Optical Absorption Techniques

The basic technique of differential optical absorption includes a radiation source emitting light that is transmitted through the sample and then measured by a detector. A detector measures the wavelength of light in the absorption band of the pollutant gas (i.e., NO_X) and a wavelength not absorbed by the pollutant gas. The Beer-Lambert Law states that the difference of the energy of the wavelengths is related to the gas concentration. The differential optical absorption technique is employed for extraction and in-situ systems.

The following section describes several specific differential optical absorption designs that are commercially available.

Optical Filters - Two optical filters are mounted near the light source. One filters light except for a wavelength, λ_0, not absorbed by NO_X molecules. The second filter allows only light of a wavelength specific to NO_X, λ_1, to pass into the gas cell. A detector measures both wavelengths of light after they pass through the gas cell (Figure 13-2).

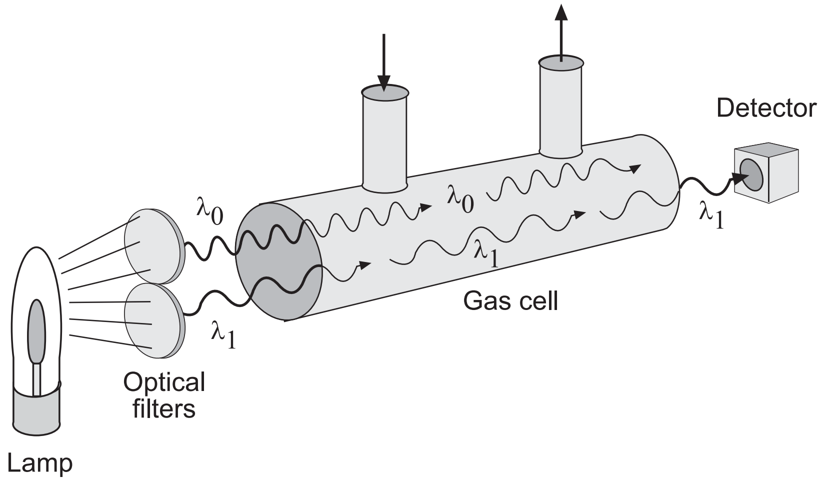


Figure 13-2. Differential optical absorption using optical filters

Moving Slit - All of the light from a source passes through the gas sample and is reflected to a rotary disk containing two slits. One slit allows light of a wavelength not specific to the pollutant gas, λ_0, to reach the detector. The other slit allows light specific to the pollutant, λ_1, to reach the detector. As the disk rotates, the detector measures the alternating λ_0 and λ_1 signals (Figure 13-3).

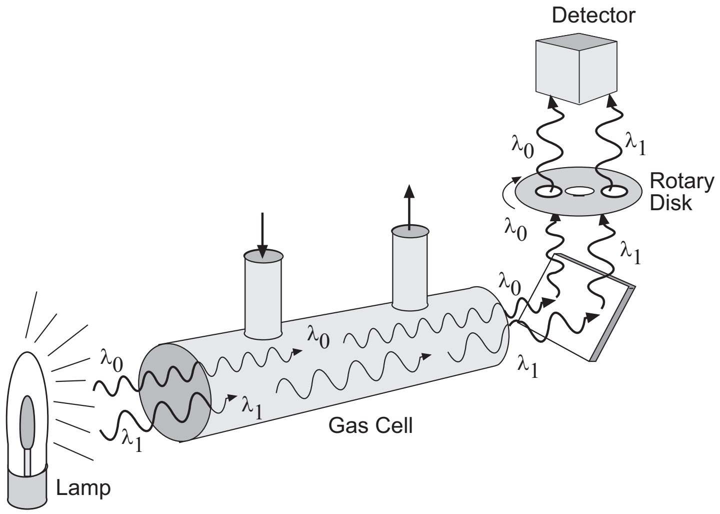


Figure 13-3. Differential optical absorption using a moving slit

Diode Array Detector - A diode array detector, shown in Figure 13-4, is a common design for in-situ systems. All of the light from a source passes through the gas sample. The light wavelengths λ_0 and λ_1 are separated by a diffraction grating, and a diode array detector measures the amount of energy for the two wavelengths.

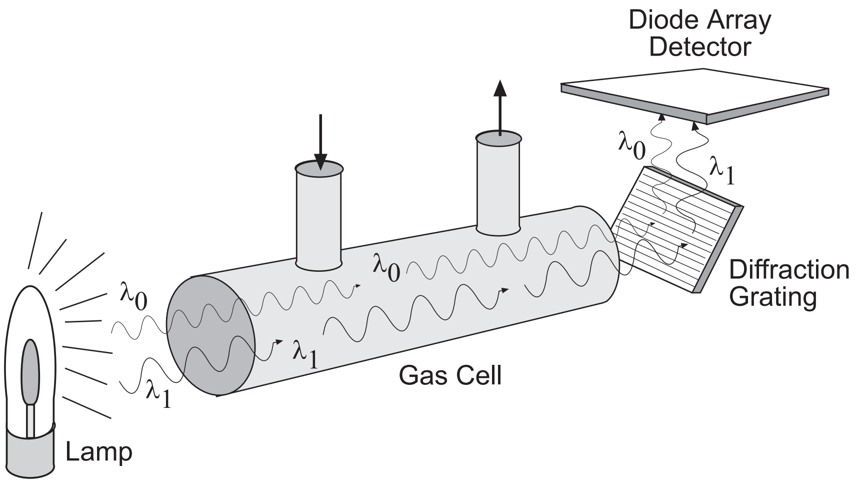


Figure 13-4. Differential optical absorption using a diode array detector

Diode Laser - A diode laser, shown in Figure 13-5, is a recent design. The light source is a diode laser that emits light of wavelengths λ_0 and λ_1. The light passes through the gas sample and is measured by a detector.

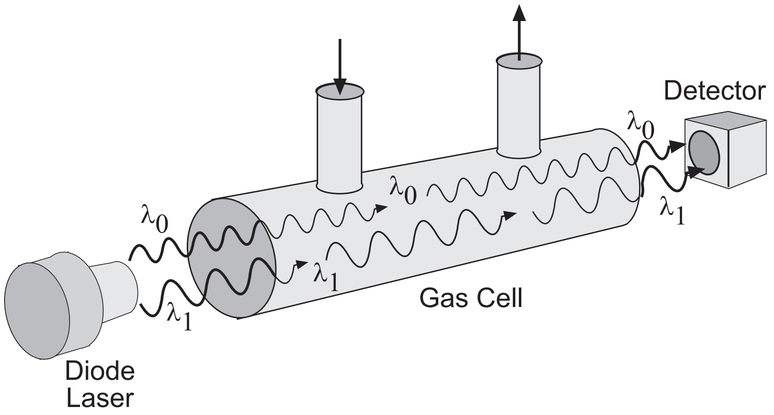


Figure 13-5. Differential optical absorption using a diode laser

Gas Filter Correlation (GFC) - GFC is applied not only to NO measurement, but also to measurement of CO_2, CO, NH_3, H_2O, HCl, SO_2 and hydrocarbons. GFC is applied to both extractive and in-situ monitors. A GFC design is shown in Figure 13-6.

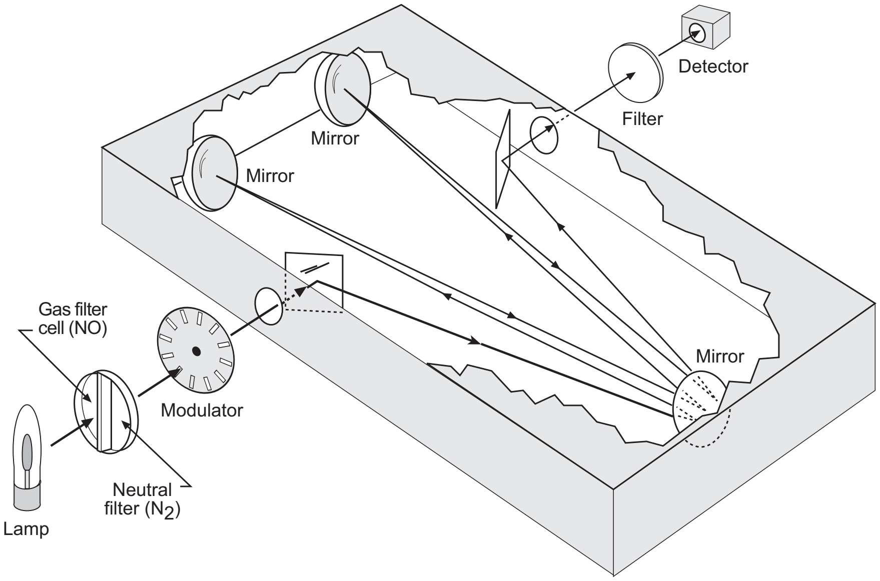


Figure 13-6. Gas filter correlation design[1]

GFC differs from other NDIR spectroscopy in that all of the reference signal energy is absorbed for the target gas compound. The infrared light emitted from a source passes through a rotating filter wheel. Half of the filter contains a neutral gas that allows the light of interest to pass through. The other half of the filter contains the target gas, which absorbs nearly all of the light at the wavelength specific to the target pollutant.

After exiting the filter wheel, the light passes through a modulator to create an alternating signal. The alternating signal then enters the sample cell where it reflects through a series of mirrors to increase the path length and improve the sensitivity of the instrument. The difference of the alternated light signals is measured to provide the gas concentration.

13.2.1.3 Polarographic Techniques

Polarographic instruments (electrochemical transducers) utilize a transducer to measure the voltage drop produced from a chemical reaction involving the target pollutant. A chemical reaction current takes place in an electrochemical cell where a selective semi-permeable membrane causes the pollutant to diffuse to an electrolytic solution. The change in current is then measured as the oxidation or reduction reaction takes place.

13.2.2 Ammonia Measurement Techniques

Ammonia monitoring methods include: chemiluminescence, IR spectroscopy, UV spectroscopy, electrochemical methods, and ion-mobility spectroscopy. One of the chief difficulties for extractive systems that monitor ammonia is the loss of ammonia in the sample lines.

13.3 CEM SYSTEMS

CEM systems are categorized in terms of the specific components and sampling techniques. Types of CEM methods include *extractive*, *in-situ*, *parametric*, and *remote sensing*. Source operating parameter monitoring is sometimes used as an alternative to an instrument-based monitoring system. *Extractive systems* are most commonly employed. Extractive systems remove a portion of the flue gas from the stack or duct for measurement of emissions.

An extractive CEM system consists of a sampling interface system, gas analyzer(s), and data acquisition/controller system. The *sample interface* system comprises all components that transport and condition the sampled gas.

One problem with extractive systems is the potential for gas loss in the system components. An option for minimizing the potential for these gas losses is the in-situ monitoring method. In-situ monitoring eliminates the need for sampling interface equipment, because they measure emissions without removing or modifying the flue gas. Measurement is made with a light source or electrochemical system (discussed in Section 13.2).

Remote *sensing* and *parameter* monitoring can eliminate the need for installed CEM systems. In parametric monitoring a parameter such as temperature, pressure drop, or fuel flow is correlated with emissions data based on a source test. The emissions data is correlated with the parametric values, using models such as a *least squares* model. This allows a program to be developed that can predict emissions based on the correlation and monitoring of the parametric values. Each system has unique advantages and disadvantages. The most appropriate CEM system is dependent on the site-specific application and regulatory requirements.

13.3.1 Overview of Systems

13.3.1.1 Extractive Systems

The sample interface system can either introduce gas to the analyzer(s) in flue gas concentrations (*source level* systems) or in a diluted form (*dilution* systems). The source level system can be either *wet* or *dry*. Depending on the specific requirements of the gas analyzer, the sample gas is introduced as either wet or dry. Water is removed from the gas sample to provide a dry sample, and removed to a lesser extent in a wet sample.

> The concentration levels of the flue gas must be within the range of the gas analyzer for source level systems. Stack gas constituents, such as particulate matter or water vapor, will cause sampling or measurement problems if not removed. Water interferes with readings for certain measurement techniques and must be removed upstream of the analyzer.
>
> Particulate matter can lead to solids buildup and plug sampling interface components or the analyzer itself. All extractive CEM systems remove particulate matter prior to measurement. If water vapor is allowed to condense on the particulate matter prior to filtering, an agglomerated material may form. Particulate matter is often removed in the sampling probe to prevent water condensation. Filtering is usually accomplished with a sintered stainless steel or ceramic filter. Filters located in the stack or duct are typically shielded from the direct flow of the flue gas stream, which prevents coarse or super coarse particulate matter from contacting the filter.

In the dilution system, the flue gas is typically diluted to a ratio 100:1 to 300:1. The sample can then be analyzed in an ambient air analyzer that is sensitive in the parts-per-billion (ppb) range. Dilution systems can be either in-stack or out-of-stack.

13.3.1.2 In-Situ Systems

In-situ systems are either *path-type* systems or *point-type* systems. In path-type systems, a beam of light is transmitted across the stack to a detector. These systems can be either *single-pass* or *double-pass*. In a single pass system the light is beamed across the stack to the detector. In a double pass system the light is beamed to a reflector that sends the beam back across the stack to the transceiver.

In point-type systems, the measurement is made within the stack over an area of about five to twelve or more inches. The measurement can be made using a light, electrochemical, or electrocatalytical sensor. The advantage of the point monitoring system is that calibration gases are readily available for daily span, zero checks, and quarterly cylinder gas audits.

13.3.1.3 Parametric Systems

There are two types of parametric monitoring methods: using *parameter surrogates* or *predictive* methods. Parameter surrogate systems do not use a lb/MMBtu or lb/hr emission limit to determine compliance, but rather a parameter (such as pressure drop across the scrubber bed) that is indicative of compliance with the emission limit. Predictive monitoring involves the use of a range of parameters that are input into a model to predict emissions. This approach can use either theory-based models or empirical models.

13.3.2 Extractive CEM Systems

13.3.2.1 Cool-Dry Systems

Cool-dry systems are the most typical extractive systems.

> For a source-level cool-dry extractive CEM system, the water vapor and particulate matter are removed prior to measurement, and readings are taken on a *dry basis*. Although the configuration differs slightly from system to system, the sampling interface generally consists of a probe, filter, conditioning system, and pump.

Figure 13-7 shows an example of a cool-dry extractive system with the conditioning system located near the analyzer. This configuration requires a heated sample line, which allows for greater accessibility to the conditioning system. A pump is used to continuously extract flue gas from the stack at a constant flow rate by. The flue gas enters a probe situated at an appropriate location inside the stack, passes through a filter, and remains heated until it reaches the conditioning system. The conditioning system, consisting of either a condensation device or permeation tubes, removes the moisture and reduces the temperature of the sample prior to analysis. It is critical to extract the water, because many analyzers have been designed for dry gases and because, as previously discussed, water can be an interferent.

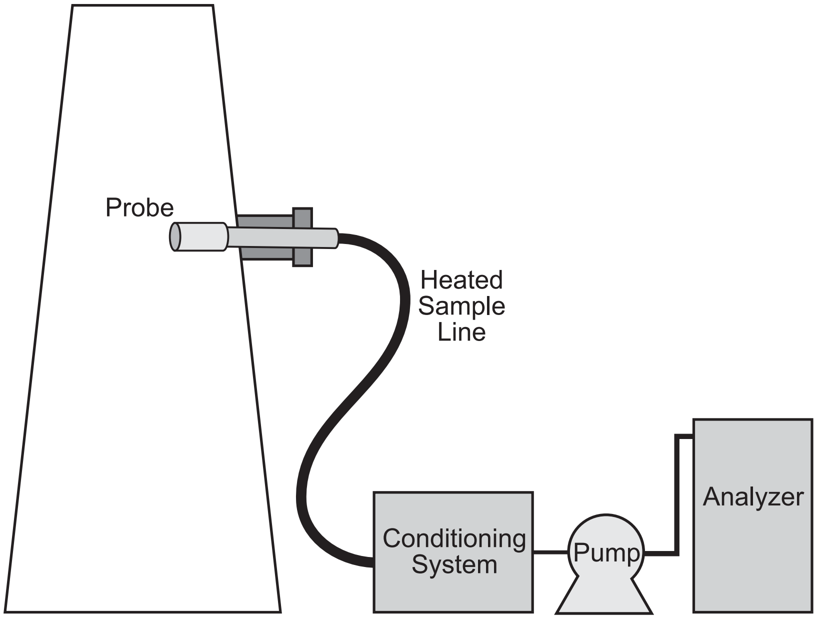


Figure 13-7. Cool-dry extractive system with conditoner

The condenser can be a mechanical refrigerator, an electric refrigerator, or a thermoelectric cooler.

Either of these devices keeps the temperature of the gas below the dew point and above the freezing point of water. As liquid collects in the condenser, it must be manually or, preferably, automatically drained. Water contact with the sample gas should always be kept at a minimum to reduce NO_2 loss.

Permeation tubes contain an ion exchange membrane to remove condensed liquid from the gas. Permeation tubes prevent gas-liquid contact; however, they may be susceptible to plugging. It is beneficial to locate the conditioning system upstream of the sampling pump. This will prevent water or acid gas condensation in the pump and lengthen its operating life.

The cool, dry, particulate-free sample is transported to the gas analyzer(s) for measurement.

The analyzer conveys analog or digital output signals to a DAS. Gas cylinders with known gas concentrations are often used during calibration to prove the CEM system is devoid of leaks and the DAS is recording accurate values.

Calibrations for almost all NO_X monitoring require the use of EPA Protocol 1 gases. These gases are certified the strict procedures outlined in the

EPA document entitled *Traceability Protocol for Establishing True Concentrations of Gases Used for Calibrations and Audits of Continuous Source Emission Monitors: Protocol 1*. EPA Protocol gases are within 1% of National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs).

NO and N_2 blends of gases are required for calibrations. Degradation of blended NO_X EPA Protocol 1 gases will occur over time. The certification period for NO/N_2 blends in aluminum cylinders is 18 months ($\geq$ 10 ppm) from the last analysis. Therefore, special attention should be given to the expiration date of calibration gases.

Because NO is a mildly corrosive gas, all metal components in contact with it must be corrosion resistant. Regulators should be of stainless steel material to minimize air diffusion and adsorption, desorption, and off-gassing.

RM testing is typically performed using a cold-dry extractive system. Infrared-based analyzers measure on a dry basis because water vapor absorbs light throughout most of the infrared spectrum.

These systems are simple in their design. Maintenance of the system consists of maintaining the heated sample lines and the plumbing to avoid leaks and corrosion problems.

Figure 13-8 shows another type of extractive system where the sampled gas is conditioned immediately upon exiting the stack or duct, making a heated line unnecessary. The conditioning system for this kind of arrangement is often less accessible for inspection and repairs. This type of system is not typically installed in the field, but more likely to be used by a source testing company.

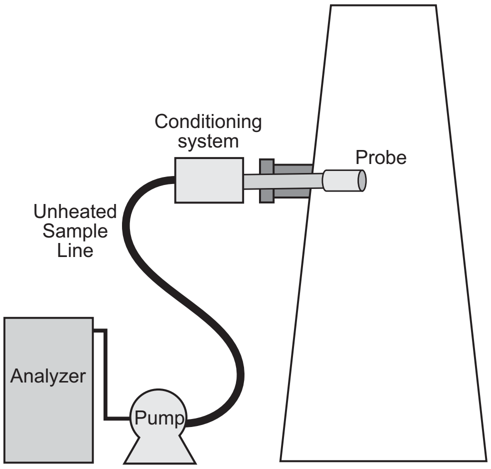


Figure 13-8. Cool-dry extractive system without conditioner

13.3.2.2 Hot-Wet Systems

Hot-wet extraction systems send the sample gas to the analyzer(s) without removal of water vapor (Figure 13-9). All components of the sample acquisition system that contact the sample must be sufficiently heated (248°F ± 25°F) to prevent condensation of water or acid gases. The heated components require routine inspection and maintenance. Components of hot-wet systems may have to be replaced periodically because heated components tend to degrade faster than unheated components.

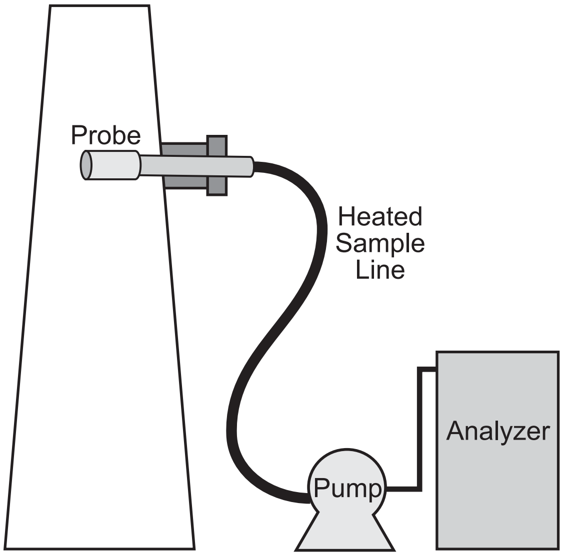


Figure 13-9. Hot-wet extractive system

Ammonia is an example of a gas that must be measured in a hot-wet manner. Ammonia will be absorbed in condensed water if the sample temperature is lowered to remove the water vapor.

13.3.2.3 Dilution Systems

The main disadvantage of source-level systems is the continual conditioning of a large volume of stack gas required. However, dilution systems require much less conditioning by sampling flue gas at a low flow rate. Flue gas is diluted either inside or outside the stack or duct. Dilution systems send either wet or dry gas containing low pollutant concentrations to the analyzer(s). However, it is often not necessary to remove water vapor because of the high dilution ratios. The analyzers generally used for these concentration levels are ambient air monitors, which are designed for lower concentrations.

In-Stack Dilution – This system consists of a dilution probe situated inside the stack. Clean, dry air is sent to the probe at a specific rate and a critical orifice usually controls the source-level sample gas. The use of the critical orifice with clean, dry air brings the temperature of the sample below the dew point so that it can be measured on a dry basis in the analyzer. Dew points of –40°F are typical. Dilution ratios are selected to accommodate the temperature.

Dilution ratios of 50:1 to 300:1 are generally achieved.[2] A dilution probe is shown in Figure 13-10.

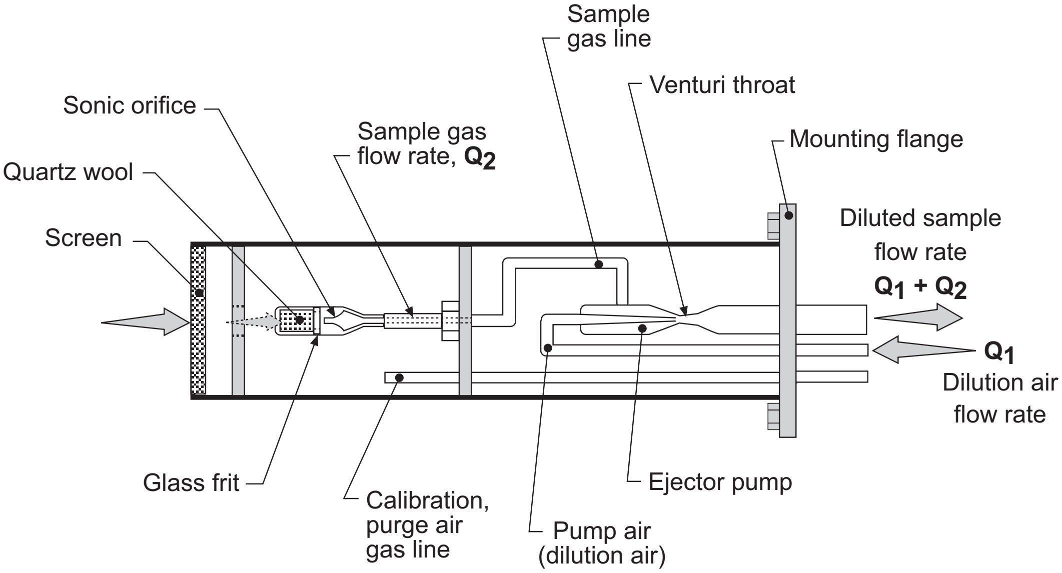


Figure 13-10. In-stack dilution probe[1]

One advantage of this system is that there is no need to remove the water from the sample prior to analyzing the gas. As a result, this system could be used with an ammonia analyzer that is sensitive enough to use with a dilution system.

On the other hand, the in-stack dilution system does not work well with stack gas containing wet, sticky particulate matter or entrained water droplets that can plug the glass frit or orifice. Out-of-stack dilution systems can provide a more accessible system for servicing.

Out-of-Stack Dilution – This system dilutes the sampled gas outside the stack or duct. Flue gas is diluted with a dilution orifice near the sampling location, at the CEM shelter, or at a location in between. A heated sample line may be used from the sampling location to the dilution assembly depending on the proximity of the dilution system to the sample probe. The dilution assembly should be located at an easily assessable location and it can be heated with a jacket to minimize condensation problems. Condensed acid gases such as sulfuric acid may corrode components of the dilution assembly. Water condensation can absorb soluble gases and create flow problems.

Out-of-stack systems have an advantage over in-stack systems, because a slipstream can be drawn from the heated sample line for oxygen determination. After dilution, the oxygen levels are too close to ambient levels to allow accurate readings.

The disadvantages of the out-of-stack dilution system include the added expense, maintenance, and inspection required for the heated components of the sample interface system. In addition, the response time for out-of-stack dilutions systems is slow because of the low flow rate of the sample through the sample line. However, the conditioning of only a small gas flow is attractive to many facilities.

13.3.2.4 Close-Coupled System

The close-coupled system is an extractive CEM design in which the gas analyzer is installed at the gas sampling location. They consist of a sample probe with a pump to transport the sample to the analyzer. A close-coupled CEM system eliminates the sampling line from the sampling interface for extractive source-level systems. The removal of the sample line minimizes problems caused by reactive, condensing, or adsorbing gases.

A disadvantage of the close-coupled system is the location of the analyzer. The analyzer can be more susceptible to environmental factors and is less accessible for inspection or repair.

13.3.3 In-Situ CEM Systems

In-situ CEM systems measure flue gas components in the stack without altering or removing flue gas. Path or point in-situ sampling systems measure the flue gas either by using a light source or by an electrochemical technique.

13.3.3.1 Point Systems

Point systems consist of a transciever and probe. The transciever sends light to a retroreflector in the probe that reflects the light back to the detector. Point systems measure the flue gas at a point or a path that is short, relative to the stack diameter (path lengths can reach 1-1½ feet in length depending on the type of instrument).

Common point systems techniques for NO_X analysis include differential absorption, gas filter correlation infrared, second derivative ultraviolet spectrometers, and electrochemical. An example of an infrared in-situ point monitor is shown in Figure 13-11.

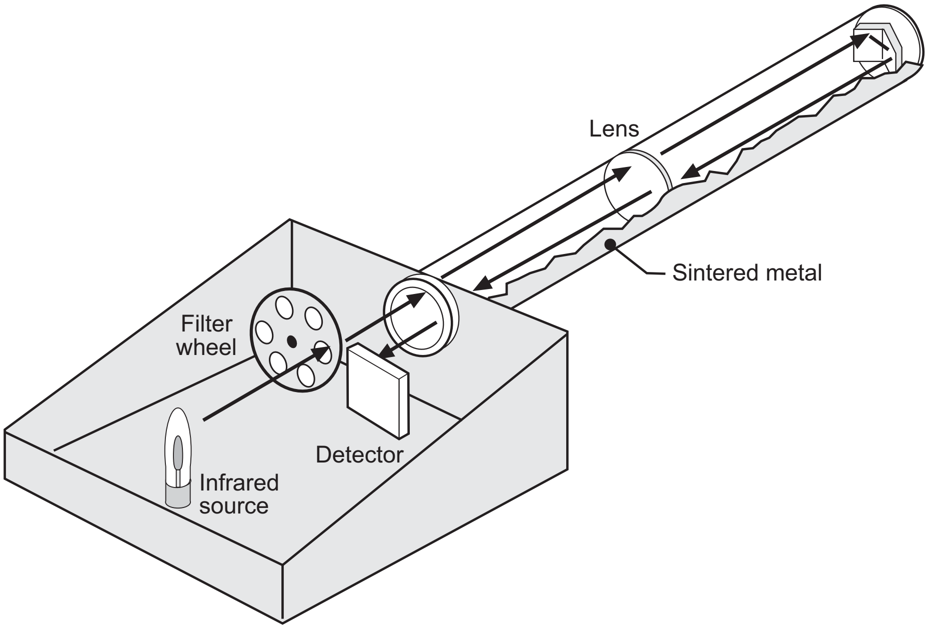


Figure 13-11. Procal UV differential absorption point in-situ monitor

Point systems can use calibration gas to calibrate the instrument by flushing flue gas out of the sensing chamber at the end of the sample probe.

Point systems are easier to calibrate than path systems because the sampling area can be flooded with calibration gas.

There are no pumps or gas conditioning system associated with these types of systems.

Point systems are susceptible to environmental factors. Problems associated with environmental factors include (1) misalignment of components, (2) loosening of circuit boards and other electrical equipment, (3) cracking of components, and (4) corrosion of components. Heavy particulate matter loading or water droplets may clog the sintered or ceramic filter protecting the sample probe. Fine particulate matter may penetrate the filter.

If the flue gas is stratified within the stack or duct point, in-situ monitoring will not provide an accurate representation of the entire flue gas stream. In-situ monitoring systems generally require less inspection and maintenance relative to extractive CEM systems. However unlike in-situ systems, analyzers and components of the extractive system can be located in a more accessible, controlled, and protective environment.

13.3.3.2 Path Systems

Path in-situ systems use optical instruments to measure the analyte across the approximate equivalent diameter of the stack or duct. A light source sends light across the path length, and a detector measures the light after it has passed though the flue gas.

> The principal measurement techniques for path in-situ CEM systems are differential absorption spectroscopy, second derivative spectroscopy, and gas filter correlation spectroscopy.

Path in-situ monitoring can be accomplished with one or two passes of the light across the flue gas.

The transmitter and the detector are located on opposite sides of the flue gas stream in single-pass systems. A double-pass system uses a retroreflector to transmit the light across the stack or duct a second time. Single-pass and double-pass in-situ monitors are shown in Figure 13-12 and Figure 13-13, respectively.

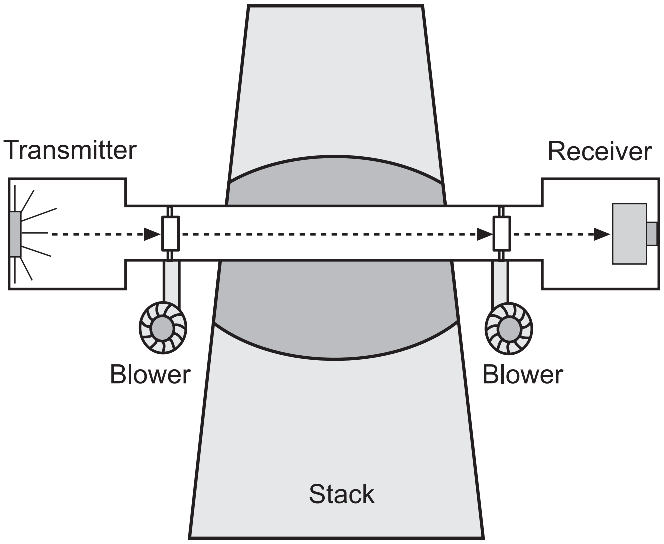


Figure 13-12. Single-pass *in situ* system

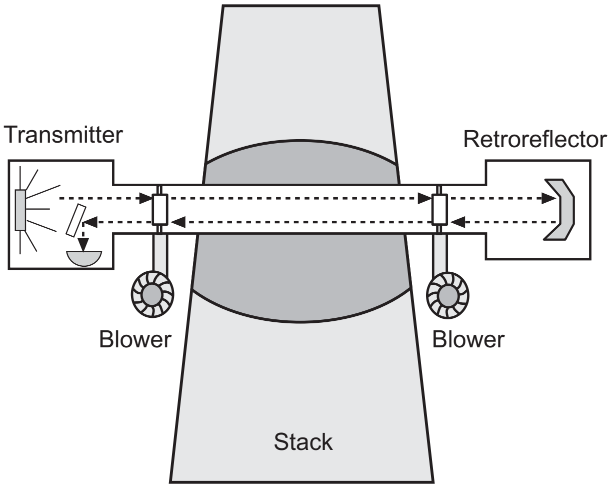


Figure 13-13. Double-pass in situ system

Path systems are advantageous for stratified sources because they sample across the entire stack or duct. In addition, problems associated with sample acquisition equipment are eliminated with path systems.

In-situ path CEM systems must be able to withstand environmental factors (e.g., weather, vibration, and temperature). The alignment of the optical components can be altered and must be checked periodically. High opacity in the flue gas caused by particulate matter or water droplets can result in low transmittance of light to the detector.

There are various methods for calibrating these systems, including checking the calibration without the use of calibration gases. Calibrations or audits with calibration gas are difficult for single-pass path systems.

13.3.4 Remote Sensing CEM Systems

Remote sensing is performed by projecting light through the plume or sensing light radiation of flue gas molecules. Remote sensing CEM systems eliminate the sample interface equipment required by extractive monitoring. Aside from opacity monitoring, commercialization of remote sensing has been limited.

13.3.5 Parameter Monitoring

Parameter monitoring uses indirect inputs to predict flue gas emissions, and can indicate the possibility that a facility is out of compliance with EPA regulatory requirements.

Parameter inputs are used as parameter surrogates, or they can be integrated into predictive emission monitoring systems (PEMS). These inputs include temperature readings, pressure readings and fuel input data. The Compliance Assurance Monitoring (CAM) program promotes the use of parametric monitoring.

PARAMETER SURROGATES

Parameter surrogates are monitored to observe the performance of air pollution control devices. A variation from the operating baseline values often indicates an increase in emissions. Operating permits may stipulate limits on control equipment during operation if emissions are not measured directly. Some of the surrogate indicators for SCR and SNCR systems are provided in the following sections.

SCR and SNCR Reagent Feed Rates and Injection Conditions - The feed rates of anhydrous ammonia (gas), aqueous ammonia (liquid), and urea (liquid) are monitored by conventional liquid or gas flow rate monitors. The feed rate should be recorded and compared with the design values for the operating rate of the combustion system. Low values indicate that the stoichiometric ratio between the reducing agent (e.g., ammonia) and the NO_X is too low; therefore, the NO_X concentrations in the stack could be high. High values indicate that excessive quantities of the reducing agent are being added, and there may be excessive “slip” emissions.

Proper distribution of the reducing agent (e.g., aqueous ammonia) is very important. This is partially dependent on the pressures in the supply headers feeding the nozzles. It is also dependent on the flow rates of the carrier streams such as preheated air for anhydrous ammonia and water for aqueous ammonia. These data should also be monitored and recorded to help operators routinely evaluate the performance of the NO_X control system.

Gas Temperatures - Both the SCR and SNCR systems have limited gas temperature operating ranges. In SCR systems, the gas temperatures at the inlet to the catalyst bed should be monitored. This data can be compared against the required temperature range for the type of catalyst being used. Low gas temperatures indicate the potential for incomplete NO_X reduction in the catalyst and the formation of corrosive ammonium bisulfate. High gas temperatures indicate the potential for damage to the catalyst.

In SNCR systems, the gas temperature at the point of reagent injection should be monitored to be in the range of 1600°F to 1900°F (870°C to 1040°C). Low gas temperatures at the injection point indicate the potential for high ammonia slip emissions. At high gas temperatures, the conversion of NO_X ceases, and the reducing agent can be oxidized to form additional NO_X. Accordingly, at high gas temperatures, the emissions of NO_X can be higher than the concentrations that would exist without reagent injection.

Gas Static Pressure Drop - After correcting these data for changes in the gas flow rate, monitoring static pressure drop provides an indication of the physical condition of the catalyst bed. Static pressures above the normal range may indicate buildup of particulate matter within the catalyst bed.

Predictive Emission Monitoring Methods

PEMS are theory-based or empirical models that correlate the parameter inputs to emissions. Unlike parameter surrogates, PEMS estimate a quantitative measurement of the flue gas emissions. A number of inputs are necessary for PEMS determination. The advantages of parameter monitoring include low initial and operating costs, low maintenance and inspection, and reduced calibration procedures.

PEMS only provide an indirect estimate of the source emissions; therefore, additional testing may be required during periods of possible noncompliance and to correlate parameter surrogates to flue gas emissions. If data applied to PEMS is not taken over an extended time period, fluctuations and other variability may bias results. Processes and gas streams differ even between similar facilities; data applicable to one facility may not be applicable to another.

Potential Problems with Parameter Monitoring

Applicability is one type of problem that can exist with parameter monitoring systems. For example, a PEMS that is based on short-term data may not be applicable to the same process on a long-term basis. Changes in the configuration or operation of the plant can necessitate the revision to the PEM to ensure that it still correlates.

Another potential problem with parametric monitoring is the validity or strength of the correlation. If a model is developed for a facility, but does not take into account all possible operations at the facility, there can be problems with the correlation. For example, if the correlation failed to account for the opening and closing of an air damper, then the correlation may not be valid when the air damper is moved from the position that it was in when the correlation was developed.

Reliability of the parameter monitoring system — to ensure reliable and accurate data over time — is another potential problem. Reliability checks of extractive systems usually consists of periodic calibration gas checks. Techniques for evaluating reliability of parameter monitoring systems are discussed in the next section.

13.4 QUALITY ASSURANCE AND QUALITY CONTROL

13.4.1 Performance Specification

EPA has established performance specifications to ensure that the CEM system (either extractive, in-situ or parametric) is producing data that are adequate for the intended purpose.

> Performance specification procedures involve a series of tests that compare known standards, or RMs, against the CEM system. Federal regulations require NSPS sources, facilities included in the Acid Rain Program, and other selected sources to permanently install and monitor CEM systems. State and local agencies may also require CEM installations through such regulations as the PSD program, Title V, and the NO_x Budget Trading Program. The type and components of the CEM system are not generally specified by these regulations. Instead the validity of the measurements of a CEM system is determined by QA/QC guidelines set forth by federal and state agencies. The most appropriate CEM system is site-specific for each facility.

To ensure that NO_X emission data are accurate and representative, the CEM system should be installed in accordance with U.S. EPA specifications in 40 CFR Part 60. The CEM system should be routinely calibrated and tested in accordance with 40 CFR Part 60 Appendix F (Appendix F), and NO_X data should be recorded and reduced in accordance with Reference Method 19.

Similar specifications are in 40 CFR 75 (Part 75) for facilities covered by the Acid Rain Program. Part 75 specifications are more stringent than for NSPS sources.

> For example, only Part 75 requires system linearity and response time tests to be performed. EPA Protocol 1 gases are required during a calibration drift test for a Part 75 source, while Part 60 sources require less stringent gas standards.

The certification of the CEM system must be performed on a case-by-case basis. One system may work on a particular stack but because of different ambient and source conditions, not on another stack. For that reason, EPA has not established a general instrument approval or certification process. Rather, EPA has required that each instrument be installed and then undergo a series of tests to determine how well the instrument is working relative to the RMs.

Performance Specifications exist for calibration drift, linearity, relative accuracy, bias (for both the analyzer and the system), and cycle time/response time. Of these, relative accuracy (RA) is the most important. The analyzers must agree with the stack test data to within ±10%. Although the requirement in the acid rain program is 10%, RA for systems installed under that program has averaged less than 5%.

NO_X CEM systems should have the capability to compile the following data necessary to confirm proper system operation.

Analyzer and Data Acquisition System

- Daily zero and span checks
- Fault lamps on the analyzer panel and/or codes on the data acquisition system
- Data acquisition system operation

Extractive Sample Conditioning System Instrumentation

- Inlet sample line temperature
- Condenser temperature
- Sample gas flow rate
- Sample pressure
- Dilution gas flow rate (if applicable)

Zero and span checks are required on a daily basis to check for instrument drift. These checks are required by 40 CFR 60.13. They are normally initiated automatically but can also be performed manually. The zero and span drift values (as indicated by the data acquisition system) should be compared against the allowable drift specifications included in Performance Specification 2 (SO_2 and NO_X CEM systems).

Most CEM systems have fault lamps that indicate if there are any mechanical or electrical problems that could be affecting the accuracy of the emissions data. In addition to these fault lamps on the front panels of the instruments, there may also be warning codes or symbols included on the data acquisition system records.

Reference Testing

The instrumental analyzer methods in 40 CFR Part 60, Appendix A are used for gaseous emissions determination and relative accuracy checks of plant-installed CEM systems. These methods are considered RMs and must pass strict requirements. RM testing requirements for NO_X CEM monitoring are found in Method 7E.

The calibration requirements for all RM testing are found in Method 6C. Prior to testing, gas standards are sent directly to the analyzer to determine that the analyzer is providing linear results that do not differ from the standards by more than 2% of the span value (upper value of the measurement range). For testing at gas turbine sources, four NO_X standards are required. For all other sources, three standards are required.

A bias check is performed prior to and following each test run. For a bias check, two NO_X gas standards are introduced in succession at the probe. The gas passes through the entire CEM system to test for possible leaks in the sample acquisition system. The recorded values for the bias check may not differ by more than 5% of the span from the concentration standards. The difference of the pre-test and post-test bias checks may not differ by more than 3% of the span. The calibration results are used to adjust test run results to account for analyzer “drift” during the run.

13.4.2 Audits

Appendix F and Part 75 require audits for CEM systems. Appendix F stipulates that an audit be performed each quarter. A facility has the option of performing a cylinder gas audit (CGA), a relative accuracy audit (RAA), or a relative accuracy test audit (RATA). A RATA must be performed at least once each year. Part 75 requires a linearity check once each quarter. A RATA must be performed either once or twice each year depending on the level of relative accuracy demonstrated.

Cylinder Gas Audit (CGA) - requires that the CEM system be challenged with NIST traceable gas standards. The gas is introduced at the sampling probe and passed through the entire CEM system.

According to Appendix F, each analyzer is challenged three times at each of two audit points. One audit point is 20% to 30% of the span value and the second audit point is 50% to 60% of the span value.

Part 75 requires four gas standards to be used during the CGA for a linearity check. The system is challenged three times at 0%, 20% to 30%, 50% to 60%, and 80% to 100% of the span value.

Relative Accuracy Audit (RAA) - only applies to facilities covered by Appendix F. The RAA is performed according to procedures stated in Performance Specification 2. Three RM test runs are performed. The relative difference between the mean of the RM values and the mean of the CEM system response determine the accuracy of the CEM system. The testing is performed while the facility is operating either 50% of maximum load or normal operating conditions. The test runs are at least 21 minutes in duration and the RM must sample at three traverse points during the test.

Relative Accuracy Test Audit (RATA) - is required to demonstrate that the system is capable of providing valid data. Data from a source test using an RM are compared against the data collected by the installed CEM system.

RATA is performed in the same manner as the RAA, except that the RATA requires nine test runs. Appendix F and Part 75 both require a RATA to be performed at least once each year. A RATA resulting in a relative accuracy of not greater than 10% for Part 75 and not greater than 20% for Appendix F demonstrate that the CEM system is capable of providing valid data. If the RA of the RATA is 7.5% to 10%, the RATA must be completed twice during the same year for facilities covered by the Acid Rain Program.

The calculations for RATAs are provided in Equations 13-2 through 13-7.

$$RA = \frac{\left|\bar{d}\right| + \left|cc\right|}{\overline{RM}} \qquad \text{Equation 13-2}$$

$$\overline{RM} = \frac{1}{n}\sum_{i=1}^{n} RM_i \qquad \text{Equation 13-3}$$

$$d_i = RM_i - CEM_i \qquad \text{Equation 13-4}$$

$$\left|\bar{d}\right| = \left|\frac{1}{n}\sum_{i=1}^{n} d_i\right| \qquad \text{Equation 13-5}$$

$$cc = t_{0.975}\frac{S_d}{\sqrt{n}} \qquad \text{Equation 13-6}$$

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \frac{1}{n}\left[\sum_{i=1}^{n} d_i\right]^2}{n-1}\right]^{\frac{1}{2}} \qquad \text{Equation 13-7}$$

Where:

RA = relative accuracy
d = difference between RM and CEM response
n = number of test runs performed
RM_i = RM value for the ith data set
CEM_i = CEM system value for ith data set
cc = confidence coefficient
$t_{0.975}$ = t-value derived in the one-tail t-test corresponding to the probability that a measured value will be biased low at the 95% level of confidence
S_d = standard deviation of the differences of the data pairs obtained during the relative accuracy test

CEM systems are considered to be *out-of-control* when they do not meet the criteria specified in 40 CFR 60 Appendix F or Part 75. A summary of out-of-control conditions for NO_X CEM systems for 40 CFR Part 60 sources and Part 75 sources is shown in Table 13-1.

Table 13-1
Out-of-Control Conditions for CEM Systems

Part 60	Part 75
Performance Specifications	
• > twice the PS drift for five consecutive days **OR** • ≥ four times PS drift	• > ± 5% of span **OR** • > ± 10 ppm for a span less than 200 ppm
Cylinder Gas Audit	
• > ± 15% of reference standard	• > ± 5% of reference standard
RAA	
• > ± 15% of RM value **OR** • ± 7.5% of the applicable standard	• Not Applicable
RATA	
• > 20% of RM value or 10% of the applicable standard • > 15% of applicable standard (for 0.30 – 0.20 lb/MMBtu standards) • > 20% of applicable standard (for <0.20 lb/MMBtu standards)	• > 20% of RM value **OR** • > ± 15 ppm for low emitters **OR** • > 0.02 lb/MMBtu

Note: RM values are in units of the emission standard

13.4.3 Summary

No type of CEM system will work properly without establishing a QA program for that system. QA begins with procurement of the system and continues throughout the life of operation of the system. The firm or organization that conducts the source testing should have a company QA program and written test procedures. The QA plan is a program of QC activities such as daily calibration, daily preventive maintenance, and checking of system pressures. The program of QC activities must be followed on a periodic basis. Ensuring that the appropriate QC procedures are followed on a regular basis can be accomplished through an audit program (either internal or external).

Another aspect of a QA program is to ensure that all objectives have been met. This includes ensuring that the data obtained from the system is representative, complete, accurate, precise and comparable to other data. Once the data is determined to meet these objectives, it can be used for the intended purpose.

Finally, it is important to note that, in addition to using the data to satisfy regulatory requirements, it can also be used for plant operation control and control equipment optimization.

13.5 OXYGEN CONCENTRATION MONITORS

13.5.1 Monitoring Oxygen Concentrations

Most combustion systems limit oxygen concentrations in order to avoid localized high concentrations in the peak temperature zones where thermal NO_X can form. However, air infiltration into the combustion system can increase to substantial levels due, in part, to the frequent thermal expansion and contraction of the combustion system during start-up, shut down, and operating rate changes. The oxygen entering with the infiltrating air can increase the thermal NO_X formation rates. Improperly adjusted burners can have oxygen levels above the intended levels causing high NO_X formation rates because of the availability of the oxygen in the peak temperature zones.

Oxygen concentrations should be monitored so that the operator can determine if factors such as air infiltration or burner operational problems could be increasing NO_X formation rates. In reviewing these data, it is important to note that the normal oxygen concentrations are a function of the combustion system operating rate. Oxygen concentrations are at a minimum at full load and increase slightly as the load is decreased due to the need for higher excess air rates at low load. Accordingly, the present oxygen concentration data should be compared against baseline data for the combustion system-operating rate (load) at the time that the oxygen data is obtained.

In reviewing the oxygen concentration data, it is also important to note that the oxygen concentrations are often not spatially uniform at the measurement location. Problems caused by air infiltration or burner adjustment can create stratified gas streams with substantial differences in oxygen concentrations. Oxygen monitors sampling gas at only one or two locations in the duct or breeching might not accurately characterize the variations in the oxygen concentration across the gas stream. Accordingly, to the extent possible, the entire breeching or duct should be sampled with an oxygen monitor.

13.5.2 Measurement Techniques

Common oxygen analyzers for extractive systems include *polarographic, electrocatalytic, magnetodynamic, magnetopneumatic,* and *thermomagnetic* analyzers.

Electrocatalytic Technique

Electrocatalytic analyzers are commonly called *fuel cell* analyzers despite the fact that fuel cells are no longer used for detection. Instead electrolytic concentration cells containing a special ceramic material are used for O_2 measurement. The ceramic material, consisting of zirconium oxide coated by a thin layer of platinum, is heated to 850°C inside a small chamber. Reference gas having an ambient level O_2 concentration is introduced to one side of the ceramic material, while the sample gas passes through the opposite side of the chamber. Mass transfer creates a flow of the O_2 molecules across the ceramic media. As the O_2 molecules pass through the platinum they are catalyzed to O^{2-} ions. Because new sample is always being passed through the chamber, equilibrium is never established. An electrode on the sample side of the chamber measures the electromotive force created by the flow of electrons. Electromotive force can be related to the concentration of oxygen in the sample as shown in Equation 13-8.

$$\text{emf} = \frac{RT}{4F} \ln \frac{P_{ref}(O_2)}{P_{sample}(O_2)} \qquad \text{Equation 13-8}$$

Where:

emf = electromotive force
R = Ideal Gas law Constant
T = temperature of chamber
$P_{ref}(O_2)$ = partial pressure of O_2 in reference side of chamber
$P_{sample}(O_2)$ = partial pressure of O_2 in sample side of chamber
F = Faraday's constant

Oxygen is one of the few gases that are *paramagnetic* (attracted to a magnetic field). Magnetodynamic, magnetopneumatic, and thermomagnetic analyzers are three common measurement devices that take advantage of the unique paramagnetic characteristic of O_2. NO and NO_2 are the only other paramagnetic gases encountered in CEM testing that, at very high concentrations, may create interference.

Magnetodynamic Technique

The magnetodynamic technique measures the deflection of a dumbbell-shaped device set in a non-uniform magnetic field. The dumbbell-shaped device consists of two diamagnetic glass spheres connected by a rod. As sample gas containing oxygen passes over the glass dumbbell in the magnetic field, the spheres are deflected. The degree of deflection is measured and related to the concentration of oxygen passing through the detector.

Magnetopneumatic Technique

In a magnetopneumatic analyzer, the sample gas is passed through an uneven magnetic field and the oxygen is drawn to the stronger side of the field. The resulting pressure differential is measured and related to the oxygen concentration.

Thermomagnetic Technique

Thermomagnetic instruments relate the paramagnetic force of O_2 to a change in temperature. Sample passes by one end of a magnetized perpendicular tube. The oxygen is attracted to the magnetic field and passes through the perpendicular tube. As sample flows through the perpendicular tube, the temperature decreases. The amount of temperature change is monitored by a change in resistance and is related to the oxygen concentration.

13.6 EMISSIONS CALCULATIONS

13.6.1 Wet and Dry Basis

As illustrated in Problem 13-1, it is necessary to report concentration values as ppm_{vd} (dry-basis) or ppm_v (wet-basis). If the difference is not specified, substantial errors in emission calculations can occur. Equation 13-9 is used to convert from a wet basis to a dry basis, and visa versa.

$$c_{dry} = \frac{c_{wet}}{(1-B_{ws})} \qquad \text{Equation 13-9}$$

Where:

c_{wet} = concentration on a wet basis (ppm_w)

c_{dry} = concentration on a dry basis (ppm_d)

B_{ws} = fraction of moisture in flue gas, $\%H_2O/100$

13.6.2 Flue Gas Correction

NO_X concentration readings can be reduced as a result of any inleakage of air throughout the process or increased excess air levels. NO_X concentration standards generally require concentration readings to be corrected using oxygen, carbon dioxide, or excess air in order to offset any dilution of the pollutant in the process. Examples of correction calculations are provided in Equations 13-10, 13-11, and 13-12.

$$C_{@7\%0_2} = C\left(\frac{20.9 - 7}{20.9 - \%\,O_2}\right) \qquad \text{Equation 13-10}$$

$$C_{@12\%C0_2} = C\left(\frac{12.0}{\%C\,O_2}\right) \qquad \text{Equation 13-11}$$

$$C_{@50\%EA} = C\left(\frac{100 + \%EA}{150}\right) \qquad \text{Equation 13-12}$$

Where:

$C_{@7\%O_2}$ = concentration corrected to 7% oxygen

$C_{@12\%CO_2}$ = concentration corrected to 12% carbon dioxide

$C_{@50\%EA}$ = concentration corrected to 50% excess air

C = concentration of pollutant in flue gas

$\%O_2$ = percentage of oxygen in flue gas

$\%CO_2$ = percentage of carbon dioxide in flue gas

%EA = percentage of excess air in flue gas

13.6.3 Mass Emission Rates

Many sources, such as those covered by Part 75, must report emissions as a mass emission rate. Mass emission rates are expressed in terms of the mass of the pollutant per unit time, which provides a more accurate indication of the amount of emissions released into the atmosphere. Equation 13-13 calculates the emissions rate based on the molecular weight of NO_2. Because NO_X quickly converts to NO_2 in the atmosphere, mass emission rates are reported as NO_2.

$$\text{Emission rate (lb NO}_X\text{/hr)} = Q_{dscfh}\ c_{dry}\left(\frac{\text{lb NO}_X}{8.375\times 10^6\ \text{scf}}\right) \qquad \text{Equation 13-13}$$

Where:

Q_{dscfh} = flow rate of flue gas at standard conditions (dscf/hr)

The dry standard flow rate of the flue gas can be calculated as shown in Equation 13-14.

$$Q_{dscfh} = A_s\ v_s\left(\frac{3600\ \text{sec}}{\text{hr}}\right)(1 - B_{ws})\left(\frac{528}{T_s}\right)\left(\frac{P_s}{29.92}\right) \qquad \text{Equation 13-14}$$

Where:

A_s = cross-sectional area of stack or duct (ft^3)

v_s = flue gas velocity (ft/sec)

T_S = stack gas temperature (°R)

P_S = absolute stack gas pressure (in Hg)

The mass emission rate can also be expressed in units of mass emissions per unit of thermal energy output (e.g., lb/MMBtu). The thermal based mass emission rate is based on the "F-factor." The F-factor is the ratio of combustion gas volume to heat content of the fuel; it varies according to the fuel used in combustion. F-factors for a variety of fuels provided in Table 13-2. The dry F-factor (F_d) does not include water for the combustion gas volume, the wet F-factor (F_w) includes all components of combustion, and the carbon F-factor (F_c) includes only carbon dioxide for the combustion gas volume.

Table 13-2
F-Factors for Various Fuels

Fuel	F_d (dscf/MMBtu)	F_w (wscf/MMBtu)	F_c (scf/MMBtu)
Anthracite Coal	10,100	10,540	1,970
Bituminous Coal	9,780	10,640	1,800
Crude Oil	9,190	10,320	1,420
Natural Gas	8,710	10,610	1,040
Propane	8,710	10,200	1,190
Wood	9,240	--	1,830

Source: 40 CFR 60 Appendix A, Method 19

Equations for emissions on a dry basis, using the oxygen-based F-factor and the carbon F-factor, are provided in Equation 13-15 and Equation 13-16, respectively.

$$\text{Emissions Rate (MMBtu/hr)} = c_{dry}\left(\frac{\text{lb NO}_x}{8.375\times10^6\ \text{scf}}\right)F_d\left(\frac{20.9}{20.9 - \%O_2}\right) \quad \text{Equation 13-15}$$

$$\text{Emissions Rate (MMBtu/hr)} = c_{dry}\left(\frac{\text{lb NO}_x}{8.375\times10^6\ \text{scf}}\right)F_c\left(\frac{100}{\%CO_2}\right) \quad \text{Equation 13-16}$$

Problem 13-1

A dilution system samples gas on a wet basis. The data acquisition system recorded an average calibration-adjusted reading of 1.25 ppm_{Vv} NO_X during the past 24-hour period. The dilution ratio is set at 150:1, and the moisture of the flue gas is 12% by volume. What is the flue gas concentration on a wet and dry basis for the previous 24-hour period?

Step 1. Determine the actual concentration of NO_X in the flue gas.

$$c = c_{measured}D_o = 1.25\ \text{ppm}_v\left(\frac{150}{1}\right) = 188\ \text{ppm}_v\ \text{(actual)}$$

Step 2. Determine the actual dry concentration of NO_X in the flue gas.

$$c = \frac{c_{wet}}{1 - B_{ws}} = \frac{188\ \text{ppm}_v}{1 - 0.12} = 214\ \text{ppm}_{vd}\ \text{(actual)}$$

Where:

D_O = dilution ratio
c_{WET} = concentration on a wet basis
B_{WS} = moisture fraction

Review Exercises

1. A facility is required to install a CEM system. The sampling source location is downstream from a fabric filter and near a breaching duct. It has been determined that the flue gas is stratified. The system must be calibrated on a regular basis. What appears to be the most appropriate CEM system for this facility?
   a. In-stack dilution sampled on a dry basis
   b. In-stack dilution sampled on a wet basis
   c. Out-of-stack dilution system
   d. In-situ double-pass path system
   e. In-situ single-pass path system
   f. In-situ point system

2. What are common problems or disadvantages of point in-situ systems? (Select all that apply.)
   a. Misalignment of optical components because of stack vibrations.
   b. Increased routine inspection, maintenance and replacement of parts compared with extraction systems.
   c. Calibration using gases is more difficult compared with path systems.
   d. Inaccessibility to filter
   e. None of the above

3. Match the CEM system with the appropriate specifications for testing and calibrations of that system.

a. Out-of-stack dilution system installed at a nitric acid facility (NSPS source)	i. 40 CFR Part 60 Appendix A
b. In-stack dilution system installed at a large electric utility facility	ii. 40 CFR Part 75
c. Source testing company RM CEM system	iii. 40 CFR Part 60 Appendix F
d. Extraction CEM system installed at an industrial steam generating source (NSPS source)	

4. An analyzer consists of an IR source that emits light through a rotating wheel. Half of the filter wheel allows gas of wavelength λ_1 to pass to the sample and half of the filter wheel does not allow gas of wavelength λ_1 to pass to the sample. The gas concentration is related to the alternating signals measured by a detector. Name this monitoring instrument.
   a. GFC
   b. Differential optical absorption using optical filters
   c. Differential optical absorption using moving slits
   d. Polargraphic
   e. Chemiluminescent

5. How are oxygen analyzers used for controlling and reporting NO_X emissions? (Select all that apply)
   a. Correct concentration values to a dry-basis
   b. Correct mass emissions rate to 7% O_2
   c. Monitor burner operation
   d. Determining air infiltration
   e. Limit thermal NO_x formation
   f. Limit fuel NO_x formation

6. The following data was obtained from extraction CEM testing performed on a 60-inch by 48-inch duct.

   1 % oxygen (dry)
   8% carbon dioxide (dry)
   9% moisture
   120 ppm NO_x (wet)
   20 ft/sec gas velocity
   242° F
   30.1 in. Hg stack pressure

   a. Determine the NO_X dry concentration corrected to 12% CO_2.
   b. Determine the NO_X emission rate in lb/hr.

References

---

[1] Jahnke, J. A. 2000. *Continuous Emission Monitoring.* Second Edition. John Wiley & Sons, Inc. New York, NY.