Assessment of Impacts of NO_x Reduction Technologies on Coal Ash Use

Volume 1: North American Perspective

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REPORT SUMMARY

This two-volume report provides documentation about physical and chemical effects combustion and post-combustion low-NO_x technologies have on coal fly ash. U.S., European, and, to a lesser degree, Japanese experience is discussed. The report assesses the effect of low-NO_x technologies on fly ash markets in a general manner. Options for beneficiating fly ash for specific markets also appear.

Background

Approximately 20% of fly ash produced in the United States is currently reused, primarily as a substitute for cement in concrete. Now, however, many U.S. utilities with coal-fired boilers are required to reduce emissions of NO_x. Methods of achieving high-combustion efficiency and low-NO_x emissions can change desirable fly ash properties (such as high-unburned carbon) that make ash attractive in a number of applications. In certain markets, these changes may preclude the use of low-NO_x fly ash. However, other parts of the world are successfully using low-NO_x ash in these markets.

Objectives

To assess the impact of low-NO_x control technologies on markets for coal fly ash.

Approach

Researchers prepared a preliminary overview of all anticipated impacts on potential ash quality that could result from low-NO_x technologies. Also appearing in the overview were a comparison of U.S. versus international experience and an examination of vendor's NO_x equipment guarantees. Preliminary information came from a survey of U.S. utilities, ash marketers, trade associations, the researchers' in-house experience, and contacts with selected international (mostly European) groups. Researchers analyzed this information to draw specific correlations, where possible, between ash quality and factors such as residence time, excess O_2, air / coal distribution, coal characteristics, efficiency of pulverizers, and additive concentrations.

Results

NO_x combustion control technologies (LNB, OFA, and so on) can increase the unburned carbon content and relative coarseness of fly ash. On the other hand, post-combustion controls

(SCR, SNCR) can cause ammonia contamination of the fly ash. Although ammonia does not impact concrete's strength, its presence generates an odor that creates nuisance conditions for workers during placement. The study found that high-carbon ash works successfully in the following applications: cement feedstock, highway construction (roadbase, subbase, asphalt filler), structural fills, physical and chemical waste stabilization, controlled density fills, mine backfill, agricultural amendments (fertilizers, soil amendments, synthetic soils), and resource recovery (carbon, cenospheres, metals). High, unburned carbon levels can adversely affect the following current fly ash uses: concrete and concrete products, blended cement, polymer fillers, grouts, and metal-matrix fillers. The report describes four approaches to minimizing the impact of reduced ash quality on ash utilization: prevention of carbon accumulation in fly ash for sensitive markets, carbon removal, concentration of reactive ash fractions by removal of coarse fractions, and ammonia removal. Volume 2 focuses on the European perspective.

EPRI Perspective

Ash sales is an important business for many utilities. It represents both revenue enhancement and reduced disposal costs. However, some utilities are currently reporting lost ash sales due to off-specification ash (high LOI, or loss on ignition) or detectable ammonia contamination. Consequently, efforts to maintain this market and even grow it in a potentially deregulated environment is critical. Pressures in this competitive marketplace suggest that any reduction in quality due to low-NO_x combustion methods will exclude ash from cement and concrete applications. To meet these demands, it will be necessary to reduce carbon content of ash for cement and concrete applications by either (1) optimizing combustion or ash collection conditions or (2) removing unburned carbon from ash through some form of post-collection materials processing. EPRI has a two-pronged approach for dealing with this issue: (1) development of new by-product uses that do not require a high-quality low carbon ash or (2) development of ash beneficiation methods.

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High ammonia ash
High carbon ash

ABSTRACT

Legislation requires many utilities with coal-fired boilers to reduce NO_x emissions. To determine the effect of low-NO_x control technologies on coal fly ash, researchers did extensive literature searches and interviews. They conducted surveys of trade associations, U.S. utilities, their own in-house knowledge bases, ash marketers, and selected European groups. From their data, they correlated fly ash quality with factors such as coal characteristics, additive concentrations, residence time, and pulverizer efficiency. Study results showed that NO_x combustion control technologies often increase fly ash's unburned carbon content, rendering it less fit for uses in concrete and its products, blended cement, polymer fills, grouts, and metal-matrix fillers. Post-combustion controls of NO_x also can contaminate fly ash with ammonia, whose odor can make working with cement unpleasant. The report describes four approaches to help decrease adverse effects of reduced ash quality. These efforts will provide coal-firing utilities with a growing base of markets for high-carbon ash.

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INTRODUCTION

This report presents the findings of a literature review conducted by Radian International LLC for the Electric Power Research Institute under Research Project 3176-17. The purpose of this report is to provide the electrical utility industry with information on the impact of current NO_x control technologies on coal ash utilization. The present study is intended to supplement the information given in EPRI's *Technology* Assessment Guide for Retrofit NO_x Controls for Coal-Fired Utility Boilers (TR-102906)[1], which provides an assessment of NO_x control technologies for wall- and tangentially-fired boilers.

Project Background

The use of NO_x reduction technologies—combustion system technologies such as low NO_x burners (LNB) or overfire air (OFA), or post-combustion system technologies such selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR)—on electric power plants has, in some cases, had a negative impact on the utilization of the coal ash in certain markets, largely as a result of increased levels of unburned carbon and other chemical residuals that are left in the ash.

The American Coal Association estimates that for 1993, almost 48-million tons of fly ash was produced.[2] Some 10.5 million tons (22%) was used rather than disposed. The largest market for coal ash is the cement and concrete industry, about 7 million tons. This market is also the highest revenue source for coal ash.

Other large volume markets for coal ash include traditional civil engineering applications in highway and construction activities as backfill. Lightweight aggregates, masonry products, and autoclaved cellular concrete are potential large volume options.

Currently about 40% of U.S. boilers have some form of NO_x control. Low-NO_x burners are the predominant technology. In Europe and Japan, combustion controls and post-combustion technologies are widely employed. With the implementation of Phase II of the 1990 Clean Air Act Amendments, more U.S. boiler will be installing NO_x control technologies.[3] For the near term, these technologies will be based on combustion modifications. In the future, new units may require post-combustion processing to meet emission limits.

Objectives

This report provides documentation, obtained from the public literature, about the physical and chemical effects seen on coal fly ash when combustion and post-combustion low-NO_x technologies are employed. U.S., European, and to a lesser degree, Japanese experience is discussed. The effect of low-NO_x technologies on fly ash markets is assessed in a general manner. Lastly, options for beneficiating fly ash for specific markets are presented.

Report Organization

Section 2 presents a summary discussion of key findings of this work. Section 3 provides background information on NO_x formation, control options, regulations, and physical and chemical properties of fly ash as it relates to current markets. Section 4 discusses experience with combustion controls. Section 5 discusses post-combustion controls. Lastly, Section 6 presents methods of ash beneficiation for certain markets.

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SUMMARY OF KEY FINDINGS AND CONCLUSIONS

Many U.S. utilities with coal-fired boilers are being required to reduce emissions of NO_x. All new facilities must meet even lower emission limits. Many older units used combustion techniques based on high single stage combustion efficiency. Under these conditions, NO_x emissions are rather high.

A number of attractive markets have developed based on the properties of fly ash produced in older boilers. Alternate methods of achieving high combustion efficiency and low-NO_x emissions can change these desirable fly ash properties. In certain markets, these changes may preclude the use of low-NO_x fly ash. In other parts of the world, low-NO_x ash is being successfully used in these markets. A review of their experience is instructional, and provides direction for ways the U.S. can increase the beneficial uses of fly ash.

Key findings of this study are as follows:

- Combustion control technologies (COM, LNB, OFA, etc.) can increase the unburned carbon content and relative coarseness of fly ash. Post-combustion controls (SCR, SNCR) can cause ammonia contamination of the fly ash.
- High unburned carbon levels can adversely affect the following current fly ash uses:
    - Concrete and concrete products.
    - Blended cement.
    - Polymer fillers.
    - Grouts.
    - Metal-matrix fillers.
- Ash with high unburned carbon levels can continue to be used successfully in the following uses:
    - Cement feedstock.
    - Highway construction (roadbase, subbase, asphalt filler).
    - Structural fills.
    - Physical and chemical waste stabilization.
    - Controlled density fills.
    - Mine backfill.

    - Agricultural amendments (fertilizers, soil amendments, synthetic soils).
    - Resource recovery (carbon, cenospheres, metals).
- Ash with high ammonia levels may not be acceptable as a cement feedstock. Concrete applications are not suitable due to the release of ammonia at high pH. Construction and other bulk applications are not impacted unless personnel exposure in enclosed spaces is possible.
- With suitable mitigation measures, low-NO_x ashes can still be used in existing pozzolan and concrete markets—albeit at a cost.
- Disposal costs for low-NO_x ash can increase due to lower bulk density. The lower density requires more water for compaction and greater volumes; landfills will not last as long.
- Methods are available for beneficiating high unburned carbon and NH_3 contaminated fly ash.

The literature review has shown little information relating fly ash characteristics to specific NO_x reduction technologies. The authors have come across many reports of higher carbon contents, higher coarseness, and ammonia contamination in low-NO_x fly ashes. The literature does not show a good understanding of exactly what characteristics of the fly ash are impacted by the different low-NO_x technologies. For the most part, the work is phenomenological and poorly documented. It is clear, however, that in some cases major problems occur with the utilization of ashes in certain applications produced by NO_x reduction processes.

3

NITROGEN OXIDES AND FLY ASH

This section discusses the interrelationship between nitrogen oxides and fly ash. The overview provides a discussion of U.S. versus international experience in NO_x regulations and trends, together with applicable NO_x reduction technology; preliminary consideration of the chemical and physical properties of ash most likely to be affected by NO_x reduction technology; and the current status of uses for ash and ash markets.

Overview of NO_x Reduction Technologies

The combustion of coal also produces the compounds NO and NO_2, collectively known as NO_x. Nitrogen is present in the fuel and also the combustion air. The dissociation of atmospheric nitrogen is a function of combustion temperature, residence time, and oxygen concentration. The formation of NO_x from fuel-bound nitrogen is not as easily correlated.

Two general classes of NO_x reduction measures are defined as 1) combustion modifications, and 2) post-combustion control technologies. Combustion modifications seek to reduce the creation of NO_x by reducing the peak flame intensity—lowering the temperature, reducing the oxygen level, etc. These changes also impact important fly ash characteristics. Typically, the unburned carbon (UBC) level in the ash increases. Lower flame temperatures also cause less ash melting. As a consequence, the ash morphology is less spherical. These changes lead to greater variability in fly ash properties that are important to ash users.

Post-combustion controls use chemical reagents (usually ammonia) to react with NO_x and reform N_2 and water. Traces of the reagents are adsorbed on the fly ash and can affect by-product markets. A common problem is the odor of ammonia when the ash is wetted.

NO_x Regulations in the U.S. and Around the World

Regulatory overviews with respect to NO_x emissions from coal-fired utility boilers in the U.S. are available from a number of sources.[1,2,3] Other useful background is given in EPRI's "Retrofit NO_x Controls for Coal-Fired Utility Boilers" assessment guide.[4] Comparative information on European regulations and limits is available from IEA Coal Research[5] and the Economic Commission for Europe's NO_x Task Force.[6]

In the U.S., the provisions of the Clean Air Act and of its Amendments, under both Title I and Title IV, affect both NO_x emissions and their controls. The Clean Air Act′s Title IV requires coal-fired boiler NO_x emissions to be cut by 2-million tons from 1980 levels by the year 2000. Title I focuses on NO_x (and VOC), and imposes compliance deadlines for ozone non-attainment areas. It requires states to revise their State Implementation Plans (SIP) so that sources of mobile and stationary ozone precursors can be controlled. Furthermore, the emission control limits should be governed by Reasonably Available Control Technology (RACT), this being defined as the lowest emission limit for NO_x that a source a capable of meeting using control technology that is reasonably available considering technological and economic feasibility. At the same time, it is stressed that significant technical, economic, and regulatory issues still remain to be resolved, thus complicating planning and the integration of compliance strategies between Titles I and IV.[1]

Under Title IV, which attempts to set the controls of pollutants associated with acid rain (SO_2, NO_x), the Clean Air Act requires that all coal-fired utility boilers with ratings greater than 25-MWe achieve compliance with NO_x emissions limits in two phases. According to EPRI[4], About 100 tangential-fired boilers, representing 32 GW capacity, and about 80 dry bottom, circular burner wall-fired boilers, representing 20 GW capacity, are included in Phase 1. All other coal-fired boilers are included in Phase 2.

U.S. Emissions Limits

40 CFR Part 60, Subpart D and Da proscribe NO_x, particulate, and SO_2 emission limits for most coal-fired boilers operating in the U.S. Individual states may require lower emission levels. Table 3-1 presents the federal limits that have been in place since 1978.

Table 3-1
Existing U.S. Federal NO_x Limits for Utility Boilers, lb/MBtu (ng/J)

	Units Placed in Service After	
Fuel	**August 17, 1971**	**September 18, 1978**
Subbituminous	0.70 (300)	0.50 (210)
Bituminous	0.70 (300)	0.60 (260)
Lignite	0.70 (300)	0.60 (260)
Lignite in Cyclone Furnace*	0.80 (340)	0.80 (340)

*When lignite is from the Dakotas or Montana.

The following annual average NO_x emission limits apply to Phase I units:

- Tangential-fired boilers: 0.45 lb / MBtu (190 ng / J); and
- Wall-fired boilers: 0.50 lb / MBtu (210 ng / J).

NO_x emission limits for other types of boilers will be set by January 1, 1997, based on the technology available at costs comparable to "low-NO_x burners." Limits for tangential- and wall-fired boilers may be also revised at that time if more effective low-NO_x technologies are available at similar costs. The NO_x compliance dates are January 1, 1995, for Phase 1 boilers, and January 1, 1997, for Phase 1 boilers also concurrently adding SO_2 control technologies. Phase 2 compliance dates and emission limits have been recently proposed by EPA.[7]

NO_x emissions are further affected by the requirements of Title I, which seeks to bring all the areas of the country into compliance with National Ambient Air Quality Standards (NAAQS) for ozone and other species. A number of areas of the United States are not currently in compliance with the ozone requirements of NAAQS, the level of non-attainment being designated from "marginal," "moderate" and "serious," to "severe" and "extreme."

Virtually all existing fossil-fuel-fired utility boilers in areas of the country that do not currently comply with NAAQS ozone standards could be affected.[4] All new sources must employ NO_x controls, and because even well-controlled new sources add to the overall NO_x burden, utilities in these non-attainment areas must reduce NO_x emissions from existing sources by an amount exceeding the projected emissions from the new unit.[4] In regions designated "moderate" or worse, existing sources must apply reasonably available control technology (RACT), the definition of which is to be established by each state, depending on the feasibility of the control technology, its cost, and the need to reduce NO_x emissions in the region. While the same NO_x emission limits as those under Title IV (i.e., 0.45 lb / MBtu and 0.50 lb / MBtu) were proposed by the EPA for tangential- and wall-fired boilers, respectively, the EPA proposes to average these over a 30-day period; some states even propose a 24-hour averaging period, making the requirements under Title I, effectively, more stringent than those under Title IV. All retrofit NO_x controls were to be in place by May 31, 1995.

European Emissions Limits

In many cases, current emission limits can be achieved through retrofit application of LNB and / or OFA. The trends to ever-tighter NO_x emission limits are expected to eventually lead to installations of post-combustion technologies such as SCR or SNCR in addition to the combustion technologies mentioned. This has already been the experience in some European countries with NO_x emission limits tighter than those in the U.S.

In Germany, a country with one of the more stringent NO_x emission standards, experience has shown that although the conversion of coal-fired plants to state-of-the-art LNBs and other combustion controls measures has been nearly completed, these "primary measures" alone cannot reduce NO_x emissions levels to their regulatory limits. "Secondary measures," namely post-combustion control technologies, are also required. This explains the phenomenal growth in the application of SCR, which appears to be the dominant post-combustion technology, both in Europe and Japan. A comparison of NO_x emission limits in different countries (Table 3-2), indicates that limits as low as 200 mg/m^3 (equivalent to 0.164 lb/MBtu) have been enacted, or are under consideration in some European countries.

U.S. NO_x Reduction Experience

As of 1990, there was an installed coal-fired electricity producing capacity of approximately 280 GWe.[4] Of that, 170 –190 GWe was built before 1971, pre-NSPS (New Source Performance Standards), without any limits on NO_x emissions. Boilers built after 1971, representing some 100 GWe of capacity, are subject to regulations on NO_x emissions as shown in Table 3-1.

Many U.S. utilities burning coal have already implemented first generation NO_x control measures. A list of utilities and their individual plants with NO_x control methodology implemented, as well as the original uncontrolled NO_x emissions, has been assembled at the U.S. Department of Energy′s Pittsburgh Energy Technology Center (DOE/PETC)[8] in February 1995.

A closer analysis of the DOE/PETC information indicates that about 113.5 GWe of U.S. generating capacity (about 40% of the total) has already implemented some NO_x control measures. Many of these were built to meet the 1971 or 1978 NSPS. Over 78% of all the low-NO_x technologies implemented in the U.S. utilities on coal-fired boilers are low-NO_x burners (LNB) or overfire air (OFA), or a combination of the two (LNB/OFA), or a combination of the LNB or OFA with other COMs. The relative share of the individual control technologies, as used today in the USA, is shown in Table 3-3.

EC Countries NO_x Reduction Experience

NO_x reduction activities in different countries, or even in individual states and provinces, depend on the current regulations in addition to the types of equipment and fuel used. NO_x control usually begins with process optimization, but as standards are getting progressively tighter, post-combustion measures are gaining in importance. Countries with more stringent emission standards, such as Germany or Austria, require flue gas treatment plants, i.e., SCR technology. Other EC countries predominately use combustion measures to abate NO_x emissions.

Table 3-2
NO_x Emissions Regulatory Limits for Coal-Fired Boilers in Selected European Countries

	Capacity	**NO_x Standard (mg/Nm^3)**		
Country	**(MW_t)**	**New**	**Existing**	**Comments**
Austria	3-50	500	--	
	50-150	400	600	
	150-300	300	450	
	300-500	200	300	Pulverized coal and stoker furnaces
		250		Fluidized bed combustion
	> 500	200	200	Pulverized coal and stoker furnaces
		250		Fluidized bed combustion
Denmark	> 50	200	Nat. Quotas	National standards for plants approved after 1/1/92
Germany	1-50	370	465	
	> 20	280	280	Fluidized bed combustion
	50-300	400	500	
			1,380	Wet bottom boilers
	> 300	200	500	
			1,380	Wet bottom boilers
			200	Unlimited life span
Italy	0-50	500-650	650	Emission standards still under discussion
	50-500		650	
	50-300	650		
	300-500	200-650		
	> 500	200	200	
		300	300	Fluidized bed combustion
Netherlands	< 300	650		Before 1/1/88
	> 300	400		
	< 300	500		1/1/90 - 1/1/92
	> 300	200		
	< 300	100		After 1/1/94
	> 300	200		
Sweden	all	80		
	150-600		270-540	As of 1/1/95, refers to the plant as a whole
	> 600		135-270	As of 1/1/95, refers to the plant as a whole
EC	< 50	650	--	Standards to be implemented by 1990
	>50	1,300	--	For existing operations reduce total NO_x emissions by 15% by 1993 and by 30% by 1998 compared to 1980 figures.

Sources: Based on References 5 and 6.

Table 3-3
NO_x Control Technologies on Coal-Fired Utility Boilers in the USA as of February 1995

Low-NO_x Technology	GWe	%
Combu5stion Technologies		
LNB	34.86	30.7
OFA	42.11	37.1
LNB/OFA	7.33	6.5
LNB/other COM	3.43	3.0
OFA/other COM	0.99	0.9
Other COM (mainly SC)	10.54	9.3
Other (mainly boiler design)/unknown	13.29	11.7
Post-combustion Technologies		
SCR (to come on stream 1996)	0.46	0.4
SNCR (demonstrations)	0.48	0.4
Total	113.49	100.0

Source: Adapted from Reference 8.

Overview of Ash Properties and Utilization

To provide a basis for comparison and to permit later assessment of the impacts of NO_x reduction technologies on ash quality and markets, the basic properties of fly ash that make it of value, together with a brief overview of the current status of ash uses and markets are discussed below.

Particulate Nature

Fly ash is a by-product of the combustion of coal in a thermal generating plant. It consists of a heterogeneous mixture of particles composed of incombustible inorganic residues and partly combusted coal. Chemically, fly ash is largely composed of compounds and minerals containing the elements: silicon, aluminum, iron, calcium, magnesium, potassium, sodium, carbon, oxygen, and sulfur. Physically, the typical sizes of particles in any sample of fly ash from modern pulverized coal fired power plants employing electrostatic precipitators (ESPs) range from below 1 :m to larger than 200 :m, with the largest mass of particulate material being between 10 to 75 :m.[9]

Particle size distributions of ash differ according to where in the dust collection system the material is collected. In ESPs, the bulk of the ash (with the broadest range of particle size) is removed in the initial electrical fields of the collection system. Closer to the ESP outlet, less material is collected, and it is of a much finer nature. Some exceptions to this observation may be made with respect to extremely vesicular particles (such as coke) that have greatly different resistivity from fly ash. In general, however, the finest particles are obtained from hoppers at the furthest collection point from the inlet plenum (i.e., ESP outlet).

The average true particle densities typically range from 2 to 3 g/cm^3 and largely reflect the chemical nature of the ashes, particularly in terms of their iron content. Bituminous coals often have significant iron content (from pyrite and similar minerals) and produce a high proportion of high density, iron-rich ash particles during combustion. However, it has been shown[10,11] that fly ash exhibits a continuous distribution of true-particle density over the range >0.8 g/cm^3 to >4.0 g/cm^3, these being the practical limits for separation of particles of different densities. This range of densities can be explained by the following factors:

- A relatively small number of particles are composite in nature (e.g., magnetite/glass, quartz/carbon combinations). These will have true-particle densities that reflect the respective material densities of the components in proportion to their mass composition.
- Some particles, such as carbon, have an internal pore structure that causes a range of density to be measured.
- By far the most important factor affecting true-particle density is the presence of large and frequently multiple closed voids in the spherical glass particles.

The measured surface area of most fly ashes lies in the range 0.5–2.0 m^2/g and, in general, the surface area increases as particle size decreases. However, the heterogeneous nature of fly ash has a major influence on surface area. Because many of the particles are spherical, their contribution to total surface area is less than that of the relatively few vesicular particles (e.g., carbon). Thus, when carbon content is high, fly ash surface area is elevated.

The color of fly ash varies over a wide range from off-white for low-iron, low-carbon ashes, through shades of beige-brown as iron content increases, to brown-black when high magnetic spinel contents are present. Carbon will generally introduce a grey shade to the ash which will darken to almost black at high levels. The perceived color is, therefore, composite in nature and will also depend on the level of magnification during observation. Color cannot be distinguished by scanning electron microscopy.

Under the scanning electron microscope (SEM), fly ash is seen to consist of a range of particles of different sizes, shapes and surface textures, although by far the most dominant in most ashes are smooth-surfaced spheres ranging in size from less than 1 :m to greater than 100 :m. The spheres are formed during the melting process which occurs during passage of the coal minerals through boiler flame.

Chemical and Mineralogical Properties

To assist in identifying those properties of fly ash which relate to "quality," it is valuable to briefly summarize some features of the chemistry and mineralogy of fly ash in a general way. Pulverized fuel fly ashes are heterogeneous mixtures of particles derived from the incombustible portion of coals. Some particles, for example quartz sand, are largely unchanged by passing through the boiler, and are captured by the gas cleaning system as discrete entities. Other particles, such as hematite and ferrite spinels of variable composition, are formed by oxidation of iron species (such as pyrite) in the coal. These, too, are sometimes collected as discrete particles, although more frequently they are produced as crystalline growths on the spherical glass particles that form the major part of most ashes.

Clay minerals comprise most of the non-combustible part of coals. During combustion, at flame temperatures of 1,500 to 1,600EC, these react and melt to form hollow or solid glassy spheres that may partly crystallize on cooling to produce mullite crystallites embedded in glass matrices. Because of their origin in common clay minerals, fly ash glasses are formed from aluminosilicate melts with SiO_2:Al_2O_3 mass ratios of the order 1.5:1. The composition of these melts, and the nature of the cooled particles, are modified by the presence of various cations, notably calcium, sodium, potassium, magnesium, and iron. The extent of modification determines the reactivity of the glasses and the nature of any crystalline phases that are precipitated during cooling and annealing.[12]

Bituminous coals are low in calcium, sodium, potassium and magnesium, though often high in iron content. When the concentrations of these potential modifier ions are low, the largely aluminosilicate melts tend to be unstable and to precipitate mullite in a matrix termed Glass I. When more cations are available, as is the case with low-rank coals, less precipitation occurs and a highly modified glass, Glass II, is formed. In extreme cases, where more cations are present than can be accommodated in the melt, crystalline components such as merwinite, melilite, tricalcium silicate, dicalcium silicate, and tricalcium aluminate are formed.[12]

Glasses are detected and characterized by XRD in relation to one or more broad diffraction features. In fly ash glasses, this generally appears as a broad diffraction maximum centered at 23–35E 22. The band position and shape are sensitive to composition. Glass I causes a relatively symmetrical diffraction maximum that is centered close to 23E 22, whereas Glass II causes a strongly asymmetric diffraction band with a maximum close to 33E 22. Some fly ashes of intermediate composition contain both glass types, both as separate particles and as mixed (phase-separated) individual particles.[13]

Most fly ashes appear to contain some water-soluble alkali and sulfate constituents. These are not normally present as distinct particles and are not usually detectable by XRD. They are probably present as surface-adsorbed species that enter solution rapidly when the ash is placed in contact with water.

Pozzolanic Reactivity

"Pozzolanic activity" is the conventional term given to the phenomenon of strength development that occurs when lime and certain aluminosilicates react at ambient temperatures in the presence of water. Through the process has received extensive study, it is by no means well understood and can be discussed only in largely phenomenological terms.

A broad division of fly ash types can be made on the basis of chemical composition[14] and the type of coal from which they originate. Those from bituminous coals, usually having low calcium, sodium, and potassium contents, are termed "Class F" ashes. Those from subbituminous coals, often with relatively high calcium, sodium and/or potassium contents, are termed "Class C" ashes. Among the Class F types, reactivity is almost totally assigned to glass phases.[15,16,17]

From the perspective of reactivity, it is possible to rank qualitatively the various particle types in fly ash in terms of their potential participation in reactions with lime and alkali hydroxides (i.e., in relation to the so-called pozzolanic reaction) as follows. Unburned coal, detrital quartz, mullite, hematite, and ferrite spinel can be considered as largely inert. Because they are present in the ash (frequently in relatively large concentrations), these components contribute to the total analytical values of silicon, aluminum, iron, and some other elements. Their presence renders bulk chemical analysis values irrelevant as a guide to understanding pozzolanic reactivity. It is generally accepted that there is little correlation between the oxide analysis of a pozzolan and its performance. From the perspective of pozzolanic reactivity, chemical composition is important only to the extent that it influences mineralogical characteristics, including most importantly, glass content.[12,16,17]

Various iron compounds may react with alkalis from ash, lime or Portland cement to form hydrated oxides, or ettringnite phases. In this respect they may be important in strength development, though probably not in relation to the pozzolanic activity normally associated with lime/silica reactions. Any tricalcium aluminate present in an ash will provide alumina at an early age. In the presence of calcium, hydroxide, and sulfate, this will form ettringnite compounds with substantial cementing capability. Tri or dicalcium silicates in ashes will also act as a cement and form calcium-silicate-hydrate. To some extent, these components can be expected to contribute to the self-cementing action of Class C ashes.

Water-soluble alkali sulfates and hydroxides are potential sources of sulfate and hydroxide ions. They contribute to the formation of gypsum and ettringnite phases, depending on the availability of aluminum. They are thus important in supporting early age cementing processes and may be significant in stimulating pozzolanic reactivity.

In most cases, the aluminosilicate glass portion of fly ash reacts as a pozzolan. A complete theory of pozzolanic activity has not yet been developed; however, there is evidence that the reactions may proceed by hydrolysis and depolymerization of the glass, involving sodium / potassium hydroxides, to form siloxane oligomers that are water soluble. These are then precipitated as calcium-silica-hydrates gels by calcium ions in solution. At the same time, alkali aluminates enter solution and may react to form ettringnite species. There is also considerable evidence that ash particles are themselves extensively hydrated, without entering solution, to form *pseudomorphic* gels of uncertain composition.[18,19] Whatever the mechanism, it is clear that pozzolanic activity and the products of hydration strongly depend on the nature of the glass in fly ash. There is also some indication that Glass II is more reactive than Glass I.[20,21] The rates of reaction in all fly ashes appear slow and the extent of pozzolanic reaction in any sample is limited, even when strength has reached levels as high as 40–50 MPa at extended ages. At early ages, mixes of fly ash and lime or cement may gain substantial strength without any indication that pozzolanic reactions have occurred at all.

In addition to these possible reactions, it is likely that other constituents of the system, such as iron, are involved in producing hydrates with cementing characteristics. Minnick has observed that lime (and magnesium oxide) can react with iron oxide in the glassy phase of fly ash.[22] However, Watt and Thorne[23] have shown that fly ashes that reacted with lime showed a progressive increase in the amounts of reacted silica and alumina, but little increase in the amount of reacted ferric oxide.

In recent work on high-volume fly ash concrete systems, Berry and Hemmings[21] have proposed that pozzolanic activity involving fly ash may be regarded as proceeding in two stages: the first, of relatively short duration, with the dominant reactions being the formation of sulfoaluminates; and the second, predominantly involving aluminosilicate hydration, accounting for late-age strength development. Though these concepts were developed to explain the activity of fly ash in Portland cement systems, it is probable that similar mechanisms prevail in other lime / sulfate environments.

Carbon in Fly Ash

Carbon has always been a common component in fly ashes produced from the combustion of fossil fuels such as coal. Carbon contents in coal ash varies over a wide range (less than 0.5% to more than 20%) depending on factors such the rank of the coal, the condition of the pulverizers, and the load conditions of the plant. For plants without NO_x reduction technologies, ash carbon levels of 5% of less are typically found in base-loaded plants burning bituminous coal. However, in contrast, carbon contents up to 10% or above are often found in non-base loaded plants, particularly those burning bituminous coals. Lower rank subbituminous and lignite coals typically have higher levels of burnout and produce ashes with much lower carbon contents. As is discussed in Section 4, with the introduction of combustion control NO_x reduction technologies carbon content can increase considerably.

Little has been published on the chemical and physical characteristics of the carbon in fly ash. In view of the importance that the carbon fraction has on the marketability of ash, this is unfortunate. Earlier work conducted for EPRI by two of the present authors[20] suggested that carbon in fly ash is quite heterogeneous and originates from at least two possible sources:

- Partly combusted coal particles, with coke-like characteristics; and
- Fine carbon with a lace-like morphology, similar to carbon-black, possibly from incompletely combusted volatile fractions of coal or carbon "cenospheres."

The partly combusted particles are typically coarse in size (>200 :m) with a considerable content of inorganic matter; the lacy carbon is of very fine size (<10 :m) with much less associated inorganic matter. As would be expected, the ash analysis of the large, partly combusted particles is similar to the original coal; whereas that for the lacy carbon is somewhat different in composition, consistent with a different origin or formation mechanism. There is an urgent need to clarify the differences in these different carbon types in ash, particularly with respect to their potential impact on the marketing of ash, including the interference with air-entrainment of fly ash concrete.

Carbon Content and LOI

Because the carbon content of ash produced under combustion NO_x control technologies is central to the study, some comments on the significance of the loss on ignition, or LOI, test for carbon determination are in order. The LOI test was originally developed to provide a laboratory means to monitor the carbon content of fly ashes as a method both of assessing combustion efficiency and determining the quality of ash for sale into the concrete market. However, it has been shown that LOI does not provide an accurate guide to the carbon content when compared with direct carbon analysis (e.g., by the LECO combustion technique).[24]

A comparison of typical data for the two techniques reveals considerable scatter, with LOI being on average some 30% higher than measured carbon content. At first consideration, the discrepancies would seem to be unexpected. The presumed relationship is based on the assumption that the only reaction involving mass loss, that might occur at ignition temperatures (typically at 750EC - 1000EC), is the oxidation of carbon to carbon dioxide. However, other reactions involving mass changes are equally possible when other components are present in the ash—some producing mass loss, others producing mass gain. The oxidation of mixed ferrous-ferric iron, typically found in ferrite spinels, is particularly problematic in this regard for ashes from bituminous coals with significant iron content. Table 3-4 summarizes some mass change reactions.

Because of the relative weighting of these additional reactions, LOI measurement must always be considered only a crude approximation of the true carbon content.

Table 3-4
Mass Change Reactions Occurring During Ignition of Fly Ash

Description	**Reaction**	**Mass Change**
Oxidation of carbon to carbon dioxide	$C + O_2$ 6 CO_2	Mass Loss
Reduction of ferric iron	Fe_2O_3 +—6 Fe or FeO or Fe_3O_4 + CO_2	Mass Loss
Oxidation of mixed ferrous-ferric iron	$2Fe_3O_4 + 0.5O_2$ 6 $3Fe_2O_3$	Mass Gain
Decomposition of calcium sulfate	$CaSO_4$ 6 $CaO + SO_3$	Mass Loss
Oxidation of sulfur or sulfide	$S / S^- + O_2$ 6 SO_2 / SO_3	Mass Loss
Volatilization of Na_2O, K_2O and other oxides, chlorides, sulfides, and decomposition of carbonates	$M_2O_{(s)}$ 6 $M_2O_{(g)}MCO_3$ 6 $MO + CO_2$	Mass Loss

Source: Adapted from Reference 24.

Desirable Properties of Ash

From the perspective of utilization and marketability, the desirable properties of fly ash are as follows:

- Particulate nature—fine size and high surface area;

- Particle shape (spherical)—flow, lubrication of mixtures;
- Reactivity—pozzolanic (Class F ash) and cementitious (Class C ash); and
- Low cost and low variability.

Clearly any changes to these properties may threaten the higher value added uses for of ash. In many low value added applications it is the soil-like (granular, particulate) characteristics that are being exploited; in others, it is the cementitious / pozzolanic characteristic.

Market Overview

According to the American Coal Ash Association (ACAA), in 1993, the last year for which a complete set of ash production and utilization data is available, based on 814-million tons of coal burned by U.S. utilities, almost 48-million tons of fly ash was produced.[9] Of this, approximately 10.5-million tons (22%) was utilized. These coal ash production and utilization figures for the USA are compared with those for other countries in Table 3-5. It can be seen that the USA is in the lower third of the countries listed but is also the second largest producer after the former USSR. China is a close third. The 22% utilization figure has been stable for a number of years after showing a strong upward trend from the mid-1960s.

Fly ash finds application in many different areas, including cement and concrete products, flowable fill, structural fill, road base or subbase, waste stabilization, mineral filler in asphalt, grouting, mining applications, and agriculture. Table 3-6 shows a breakdown of fly ash production and uses, viewed in terms of "external" market applications (total 9.87-million tons) and "internal" producer applications (total 0.64-million tons). Both views clearly show the dominance of the cement and concrete markets for fly ash. In 1993, out of the total 10.5-million tons of ash used, almost 6.8-million tons was utilized by the cement and concrete industry. In other words, the share of the cement and concrete industry in fly ash utilization represented almost 65 percent. Changes in the quality of the ash that would prevent utilization in either the cement or concrete products would, therefore, have a significant impact on the total utilization of fly ash.

More detailed information on these and other issues relating to ash utilization can be found in the eleven ACAA / EPRI International Symposia on Use and Management of Coal Combustion By-Products, given between 1967 and 1995.[25]

Table 3-5
Coal Ash Production and Utilization: Worldwide Data and Ranking (KT/Y)

Country	Fly Ash Production	Total Ash Production	Utilization	% Utilization
Netherlands	815	900	940	>100*
Denmark	840	980	880	90
Belgium	930	1,090	795	73
Italy	1,300	1,435	900	63
Germany (FRG)	7,480	11,600	6,485	56
France	2,200	2,605	1,300	50
Japan	3,480	3,925	1,920	49
UK	9,950	12,540	6,120	49
Germany (GDR)	--	19,100	7,200	38
Canada	3,830	5,250	1,575	30
China	--	62,500	16,200	26
Austria	375	400	100	25
Finland	640	710	180	25
U SA	48,430	65,190	15,895	24
Sweden	300	490	100	20
India	--	40,000	6,750	17
Poland	--	29,500	4,500	15
Spain	7,390	8,695	1,220	14
Australia	7,050	7,900	800	10
USSR (former)	--	125,000	11,500	9
South Africa	--	13,000	580	4

*Some ash is imported.
Source: Adapted from Reference 5.

Table 3-6
U.S. Fly Ash Production and Utilization, 1993 (Short Tons)

Fly Ash Production	**47,756,492**
Fly Ash Uses	
External Market Applications	
Cement and Concrete Products	6,791,608
Flowable Fill	336,390
Structural Fill	669,215
Road Base / Subbase	947,603
Mineral Filler in Asphalt	108,286
Snow and Ice Control	608
Grouting	16,437
Coal Mining Applications	18,708
Waste Stabilization	437,676
Miscellaneous / Other	544,057
Subtotal–External Market Applications	9,870,588
Internal Producer Applications	
Flowable Fill	44,059
Structural Fill	242,268
Road Base / Subbase	58,802
Miscellaneous / Other	292,107
Subtotal–Internal Producer Applications	637,236
Total Applications	10,507,824
Use as a Percentage of Production [%]	22

Source: Reference 9.

Fly Ash Use in Cement and Concrete

The total of 6.8-million tons sold to the cement and concrete market is not usually disaggregated by industry into its two main component parts: cement manufacture (raw meal for clinker), and use as pozzolan in concrete. The use of ash in blended cement is strictly a concrete pozzolan use and should be carefully differentiated from the manufacture of Portland cement clinker. While ACAA does not disaggregate the cement vs. concrete utilization of fly ash, it is generally understood, that use of fly ash in concrete represents a much higher share than fly ash in cement production. One major utility that sells about 5-million tons of ash annually, ships 60% of its production to the concrete manufacturers versus 20% to the cement producers, with the remaining 20% for other applications. This utility accounts for over half of the ash marketed in the country.[26]

In terms of product cost, the geographic location of the ash is always of major consideration, and it is tied strongly to regional construction industry activities. For these reasons, ash sells over a wide price range ($30-80 per ton). With ready access to water transportation, it is possible to economically ship ash long distances. In addition to concrete, considerable quantities of ash are also used in backfill cement in the hardrock mining industry.

The blended cement and concrete pozzolan markets require fly ash to have:

- Low carbon content (LOI) to reduce admixture (air entraining agents and superplasticizers) demand and product color;
- Maximum pozzolanic activity; and
- Minimum property variability.

ASTM C618 currently specifies a 6% maximum LOI (not carbon content) for fly ash as a cement admixture, although local state and other users usually do not allow higher than 4% LOI. In some areas, even an LOI value higher than 3% is unacceptable. However, ASTM C618 is under review and specifications for ash LOI are undergoing change. Some ash purchasers are setting much lower limits in the form of performance standards (e.g., less than 3% to 4%). These properties should be recalled when considering the case studies and reports of NO_x reduction technologies identified in Sections 4 and 5.

Development of New Markets

The development of additional markets for ash has been an ongoing effort by utilities and ash marketers for some 30 years. There are a number of potential applications for which ash is well suited technically but which, for various reasons, are currently not yet well developed. These mostly include high volume construction uses (e.g., flowable and structural fills, road base or subbase, waste stabilization, mine backfill, agriculture, etc.) which are typically low value added uses where the ash serves as a replacement material for soil, fine aggregate, borrow materials, or the like. Although less desirable than the concrete market, they are nevertheless attractive options that offset the costs of disposal. Efforts in this direction will require a concerted effort by the industry to develop national standards and codes which specify the use of ash for these types of applications.

Anticipated Impacts of NO_x Reduction Technologies on Fly Ash Quality

There are six areas in which the properties of fly ash are potentially affected by the current generation of combustion and post-combustion NO_x reduction technologies. Each is discussed below.

Increased Carbon Content

As will be discussed in more detail in Section 4, the main potential problem with fly ash originating from various COM / OFA and particularly from LNB equipped coal-fired boilers is their increased unburned carbon (UBC) content.[27] Depending on the type of furnace, burner technology, and operating parameters, UBC may increase by 0.5 to 10 percentage points, making such fly ash unusable for applications such as blended cements and concrete where interference with air entrainment, water demand, strength, and workability are major concerns. Other applications, however, may not be sensitive to increased carbon levels, a good example being the production of cement clinker or sintered lightweight aggregate since the carbon is burned during processing. Carbon contamination is a major issue for coal ash utilization and was the subject of a recent DOE / PETC Conference.[28]

Particle Properties

Properties which potentially could be affected include the size distribution, relative coarseness, and shape / morphology. With an increase in UBC, combustion control systems can be expected to generally increase the percentage of coarse particles in an ash. There may also be some general coarsening of the size of the inorganic constituents through changes in the rate of gas evolution during combustion of the coal particles, leading to foaming and particles with more irregular, vesicular shapes compared to the normal spherical shape.

Mineralogical Properties

Other differences can be expected in the state of mineralization in the ash particles as a result of different residence times as the ash particles pass through the boiler flame and into the dust collection system. Longer residence times or different thermal histories in the flame can allow more time for the quenching of the glassy particles, a process which will produce lower total glass contents and probably different glass types.

Reactivity

The inherent reactivity of a given ash, regardless of whether it is pozzolanic activity or self-cementing capacity, depends largely on the state of mineralization (essentially the aluminosilicate glass content) and / or the presence of hydraulic crystalline phases. The particle size distribution and surface area essentially control the rate of the reactions. Any changes in the mineralization or the particle size distribution will naturally be expected have an impact on the reactivity of an ash.

Variability

Variability in an ash (e.g., in fineness, composition, reactivity, color, etc.) has always been a marketing problem. Considerable efforts have been made by marketers to select sources with low variability to permit the sale of "quality assured" ash products. Any increases in variability accompanying the installation of NO_x reduction technologies may cause problems in retaining these markets, particularly faced with competition from quality controlled competitive materials such as blast-furnace slag.

Contamination with Ammonia

A quite distinct ash problem, this one associated with the post-combustion NO_x reduction technologies, is the presence of ammonia. Both SCR and SNCR post-combustion NO_x reduction technologies utilize NH_3 from such agents as ammonia or urea to reduce NO_x to N_2. Not all injected reagent is consumed in the reactions connected with NO_x reduction. Unreacted ammonia, usually called "ammonia slip," passes with the flue gases through the system, a large part of it being deposited as ammonium bisulfate in the fly ash collected in the electrostatic precipitator, and a smaller part leaving the plant through the stack.[5] While estimates differ, it is usually assumed that as much as 70–80% of the unreacted ammonia is retained in the fly ash.

Ammonia contamination of ash represents a potential problem in both the cement and concrete applications areas. Experience to date in North America with ammonia-contaminated ash has come largely from plants using it as a precipitator aid. In many cases, ash from these sites was unmarketable. Although post combustion NO_x processes will likely lead to much lower levels of ammonia contamination, it is likely that ash marketers will be very wary of a given source until it is demonstrated that the level of contamination is both stable and below a certain critical level (to be determined).

Whether ammonia contamination also leads to problems with ash disposal will also have to be addressed.

Beneficiation

While considering which properties of ash may be affected by NO_x reduction technologies, it is useful to introduce the concept of ash property upgrading, or beneficiation, which could be used as a means of preserving existing markets by improving the quality of an ash. Upgrading could be as simple as particle size control, or more technically demanding such as carbon or ammonia reduction/removal. There is a considerable amount of commercial and research experience with methods for ash upgrading which could be applied to improving the quality of ashes from NO_x reduction technologies. These activities offer the attractive proposition of opening up other opportunities for revenue enhancement for the utility, while at the same time offsetting disposal costs. This topic is addressed in Section 6.

4

COMBUSTION TECHNOLOGIES

This section summarizes the types of combustion system NO_x reduction technologies used by the electrical power industry, drawing on appropriate data from worldwide sources with particular emphasis on their potential impact on ash quality. This information has been analyzed with a view to comparing quality and factors such as: residence time, excess O_2, air/coal distribution, coal properties (characteristics), efficiency of pulverizers, additive concentrations, etc. These data are related to U.S. and world (especially European) operating experiences and practices.

Information has also been collected on the characteristics (where known or reported) of the coal ash resulting from LNB retrofit technologies. Important ash characteristics include: the carbon content and its nature; chemical, physical and mineralogical properties, including particle size distribution, surface area, glass content and glass chemistry, and the presence of other "impurities;" variability; and pozzolanic activity and self-cementing properties. Where available, information has also been gathered on experience gained on the effect and limitations of using low-NO_x ashes in concrete and other applications.

Combustion NO_x Controls

The first steps to control and reduce NO_x emissions normally involve combustion operation and design/burner modifications. Combustion modifications, also called primary NO_x reduction measures, have been under continuous development and optimization, and can be divided into three generations, following the classification given by the Economic Commission for Europe (ECE) "NO_x Task Force”:[1]

First Generation:

Low excess air (LEA);
Mills or burners-out-of-service (MOOS or BOOS); and
Biased-firing.

Second Generation:

Low-NO_x burners (LNB) (air staging at burner);
Flue gas recirculation at burner (FGR); and
Overfire air (OFA).

Third Generation:

Low-NO_x burners (LNB) (air and fuel staging at burner); and
Reburning or in-furnace NO_x reduction (IFNR).

The first generation comprises those measures which do not require major changes to the firing system. They are simple and economical measures for use in retrofit. The measures of the second generation aim at increasing the devolatization of fuel nitrogen and simultaneously reducing the atomic oxygen availability in the primary zone of the burner, thus reducing peak temperatures. Low-NO_x burners can be collectively defined as burners with integrated air-, fuel-, or air-and-fuel staging. The concept of the LNBs can also be achieved for existing burners by means of additional mechanical changes. The third generation also includes those measures, which reduce NO_x already formed at the burner or in the boiler. The combustion modifications of the second and third generations can be applied in the boiler and / or to the burner. In reality, combinations of both are often used.

Another option showing some promise appears to be an advanced staged combustion technology, or reburning. In this technology, the primary burner is allowed to operate under "normal" excess air conditions, firing ~85% of the total boiler fuel input. The remaining 15% of the fuel is injected above the primary zone with a deficiency of combustion air to create a fuel-rich reburning zone where the majority of the NO_x reduction occurs. A final "burnout" zone is created by the injection of the remaining combustion air. The reburn fuel can be virtually any hydrocarbon, including gas, oil, and coals of all types.[2,3] This technology has been demonstrated at several U.S. utilities and is discussed in more detail below.

The application of combustion modifications is limited by operational and fuel specific parameters, which influence safe plant operation, such as:

- Ignition stability at burner;
- Problems of corrosion or abrasion, especially with high chloride coal;
- Slagging and ash flow in wet bottom boilers;
- Burnout (i.e., increased content of unburned carbon in fly ash);
- Increase in CO concentration;
- Changes in water-steam circuits; and
- Changes in flue gas temperatures.

It is obvious that the choice of a combustion modification and the resulting effects are site specific, and are not directly transferable from one plant to another.[1]

Practical experience with various combustion NO_x measures, their performance (i.e., NO_x reduction), and the impact on boiler operation and maintenance have been reviewed and discussed in a number of publications, meetings, conferences and workshops. The basic description and discussion of various NO_x controls is well described in three publications published by EPRI[4], IEA Coal Research (IEACR)[5], and the Economic Commission for Europe (ECE).[1] The best source of more detailed information and discussion of the U.S. experience are probably the proceedings of the biennial EPA/EPRI Joint Symposia on Stationary Combustion NO_x Control.

The two combustion NO_x controls that industry has the widest experience with and that are practiced by many U.S. and world utilities include:

- Burner configuration modifications, that include low-NO_x burners (LNB) used on wall fired-boilers, and coal/air nozzle modifications (C/ANM) as implemented on tangential-fired boilers; and
- Windbox configuration modifications called overfire air (OFA), where additional air ports are added above the top row of burners so that some of the secondary air is diverted from the primary combustion zone to this area for combustion completion. Depending on the type and configuration of the boiler, OFA can appear in different arrangements.

Combustion NO_x controls as defined and used in this study follow closely the definitions used in EPRI's *Retrofit NO_x Controls for Coal-Fired Utility Boilers, A Technology Assessment Guide for Meeting Requirements of the 1990 CAAA*.[4] These definitions are presented in Table 4-1.

Impacts of Combustion Controls

The following sections discuss some of the impacts of combustion controls on fly ash properties.

Coal Properties

Coal reactivity, usually expressed as volatile matter or fixed carbon-to-volatile matter ratio, is the primary coal property affecting NO_x emissions and UBC. Coals with good burnout characteristics (e.g., western coals) typically have low UBC under conventional firing and exhibit little change following combustion NO_x control retrofits.[4] However, coals that already produce excessive UBC under conventional firing, such as many eastern bituminous coals, and those fired in compactly designed boilers are expected to experience post-retrofit UBC increases as much as a doubling. A typical baseline UBC level is 1–3% for western coals, and 2–6% for eastern bituminous coals.

Table 4-1
Definitions of Terms

Burner Configuration Modifications	
Low-NO_x Burners (LNB)	A burner specifically designed to reduce NO_x formation, and used mainly in the utility industry in wall-fired boilers. The underlying concept, applied in many variations, is that of stepwise combustion (i.e., in successive stages). In stepwise combustion, delayed mixing and the input of fuel and air at appropriate stages achieve a controlled combustion process with a fuel-rich flame core and lowered peak temperatures.
Coal/Air Nozzle Modifications (C/ANM)	This term is used with respect to the redesign or resizing of coal and/or air nozzles in tangential-fired boilers, and it includes a range of supplier-specific staging techniques such as ABB C-E's concentric firing system and FW's TLN Burner. Coal/air nozzle modifications are physically analogous to low-NO_x burners in that they stage combustion within the flame.
Windbox Configuration Modifications/Overfire Air	
Overfire Air (OFA)	OFA is a NO_x control technology in which a portion of the secondary air is diverted to injection ports/compartments located above the primary combustion zone, thereby reducing available O_2 in the primary combustion zone. Tangential-fired boilers use two variations of this technique: close-coupled OFA and separated OFA. OFA implemented in wall-fired boilers is similar to separated OFA for the tangential-fired ones.
Separated OFA (SOFA)	OFA installed separate from and above existing wind boxes in tangential-fired boilers. This approach is the same as OFA in wall-fired boilers in that it involves new water-wall penetrations to accommodate placement of the OFA ports (wall-fired boilers)/compartments (tangential-fired boilers).
Close-Coupled OFA (CCOFA)	In this arrangement, OFA is installed within, and at the top of, the windbox in tangential-fired boilers. There is no physical space for CCOFA in wall-fired boilers.

Source: Based on References 4 and 5.

Coal Fineness

Experience has shown that where the capacity exists, reducing the size of coal particles (especially increasing the proportion of material passing a 50-mesh [300 mm] screen) can mitigate potential increases in UBC.[4] A fine grind improves the burnout rate due to the increased surface area of the fuel. This either results in an improvement in burnout or allows for changes to the combustion adjustments, such as lower stoichiometry at the burner for NO_x reduction.[1] Finer particles can also cause an indirect decrease in NO_x formation by enabling lower excess air operation while maintaining flame stability and an acceptable content of UBC in the fly ash.[5] However, this is not without a penalty. There have been reports of a 1.5% decrease in pulverizer capacity for every 1% increase in <50 mesh fraction[6]; and in most cases, the improved grinding will also result in higher power consumption, with the finer particles reducing the collection efficiency of the ESP.[5]

When firing coal mixtures, the burnout problem may be magnified. For mixtures of both high and low volatile coals, the high volatile coal ignites and burns faster than the low volatile coal. As a result, low volatile coals must burn in an O_2 low atmosphere, resulting in higher UBC.[1]

Unburned Carbon

One of the factors that many of the combustion NO_x controls have in common is increased content of unburned carbon in the resulting fly ash. Unburned carbon means significant fuel wastage to the utility, and as such is a factor in boiler combustion efficiency. (Lower stack gas heat losses affect this effect to some extent.)

This unburned carbon (UBC), unless corrected by other measures, is collected together with other particulate matter in the electrostatic precipitators. Experience has shown that UBC in such fly ashes can be as much as 2–2.5-times higher than in ashes from boilers with no combustion NO_x controls in place. Higher UBC levels can affect the marketability of fly ash, resulting in a loss of ash sale revenues and a disposal cost to the utility (depending on the region of the country, approximately $10/ton).[4] Other sources provide much higher disposal costs ranging from $12/ton up to $65/ton in Northeast U.S., with an average in the $20–25/ton.[7]

As noted in Section 3, it is common in the literature to find unburned carbon (UBC) in fly ash approximated by loss on ignition (LOI). However, LOI, apart from unburned carbon, also includes positive (mass loss) contributions from sulfates and negative (mass increase) contributions from iron phases (such as ferrite spinel) present in the ash.[8] Significant errors can therefore occur, and caution with interpretation is required, whenever LOI is interpreted to mean carbon in the ash.

Oxygen Level

As already noted, reduced O_2 levels while benefiting NO_x emissions, increase carbon content in fly ash. The unit heat depends on the tradeoff of lower stack losses and less efficient fuel consumption.

Other Changes in Fly Ash Characteristics

The increases in the unburned carbon content, even if in at least some cases it appears to be feasible to counteract these through coal (finer grinding) and combustion operation adjustments, is only a part of the problem. Other potential changes in ash characteristics and properties attributable to combustion NO_x controls include:

- Changes in the shape of the fly ash particles, these being less spherical;
- Different morphology of the ash compared to the conventional ash;
- Differences in particle size distribution, lower content of fine particles (< 10 mm);
- Differences in surface area, ash particles more agglomerated;
- Ash particles more porous;
- Differences in glass content of fly ash;
- Differences in the type and activity of carbon present in ash; and
- Changes in pozzolanic activity.

These differences in the ash characteristics, even if the UBC can be controlled within the specifications, can cause problems with high-grade ash applications in cement and concrete due to:

- Higher water/cement ratio; ultimately, increased water demand demonstrates itself in lower strength of the concrete; and
- Deterioration of the superior workability normally associated with the fly ash.

U.S. Experience

The following discussions are based on reported results prior to 1994.

Simulations

To quantify the effects of combustion parameters on NO_x reduction and on LOI, a series of experiments were conducted at Consol′s research combustor.[9] The trade-off between reduced NO_x levels and increased LOI, already reported by other researchers and confirmed in practice, was observed here as well. However, it was found that LOI was less sensitive than NO_x to variations in burner parameters, which could be manipulated to produce low levels of both NO_x emissions and acceptable LOI. Finer coal feeds, again in agreement with the results of others, reduced LOI and showed no significant effect on NO_x emissions.

Experience from actual field combustion NO_x control from either demonstration or commercial retrofits has been summarized by EPRI.[1] It is concluded there that while no significant increases in UBC are expected with higher reactivity coals, increases of 3 to 5 percentage points can be anticipated with less-reactive, eastern bituminous coals. In some OFA / SOFA retrofits, UBC increases of 5 to 10 percentage points for these eastern coals have been observed. With increases in UBC, adverse impacts on ESP performance may result, and where UBC increases above the level required for ash sales, an ash disposal problem may also occur.

Wall-Fired Boilers

A number of wall-fired boilers burning less-reactive eastern coals, including Hammond 4[10,11,12] Gaston 2[12], Sammis 6[13], Homer City 2[14,15], and Edgewater 4, reported increases in UBC. Boilers burning western bituminous coals, such as Four Corners 4,[16,17] and Cherokee 3,[2,3] showed insignificant changes in UBC. Table 4-2 provides a summary of NO_x reduction and LOI increases observed and reported in the literature from early demonstrations of low-NO_x burners.

Hammond 4. Hammond 4, is perhaps the best documented U.S. combustion NO_x control (DOE Clean Coal Technology demonstration project) retrofit. Southern Company has conducted demonstrations of a number of advanced NO_x control technologies applicable to wall-fired boilers, including advanced OFA, LNB, and combined AOFA / LNB. Figure 4-1 shows data for LOI as affected by various NO_x combustion control measures, at full-load condition, as well as at a reduced load. While the full-load LOI baseline is about 5%, it increased to 8% with LNB alone, to 10% with OFA alone, and to 11% with LNB coupled with OFA.[4,12]

Gaston 2. Figure 4-2 plots Gaston 2 results where LOI was measured during each of the first three performance tests at loads of 260, 185, and 135 MW. Fly ash LOI increased at all loads following the LNB retrofit. At full-load, LOI increased from about 7% to 11 percent. Not surprisingly, in both operations LOI decreased when running at less than full-load.

Homer City 2. LOI levels in the fly ash were initially measured in the 15–20% range, as compared to <3% prior to the burner retrofit. Improvements in coal fineness and coal flow balancing led to a reduction in LOI down to the 5–12% range. This LOI range is high, making most of the ash unmarketable. At Homer City it was concluded that any further reduction in LOI levels would require redesign of the split flame tips to allow the burners to operate at more optimal primary air velocities.[14]

Table 4-2
NO_x Reduction and LOI Increases in Wall-Fired Boilers—U.S. Operating Experience

Unit Name	**NO_x Reduction Technology**	**Type of Coal**	**NO_x Reduction (%)**	**LOI Increase/ Decrease (%)**
Cherokee 3 PSCC	LNB LNB + reburning	Western Bituminous	35–40 65	2% increase 0.5% increase
Four Corners 4 Arizona Publ. S.	LNB	Subbituminous	55	no data
Edgewater 4 Ohio Edison	LNB	Eastern Bituminous	50	increase
Gaston 2 Alabama Power	LNB	Eastern Bituminous	45–50	initially 3% increase offset by classifier upgrade
Hammond 4 Georgia Power	LNB OFA LNB + OFA	Eastern Bituminous	45–50 15–30 55	3-5% increase 3-5% increase 5-7% increase
Homer City 2 PENELEC	LNB	Eastern Bituminous	45–60	5 - 10% increase
Sammis 6 Ohio Edison	LNB + OFA	Eastern Bituminous	65–70	up to 4% increase at 70% reduction
Wabash River 5 PSI	LNB	Eastern Bituminous	uncertain (no baseline)	reduction

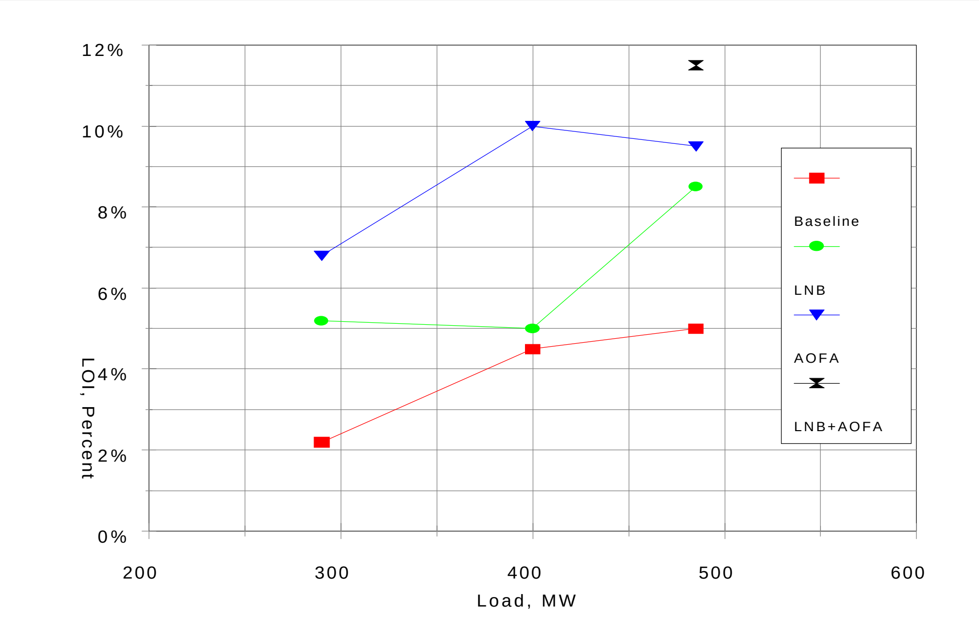

Figure 4-1 Effect of LNB and / or OFA on LOI in Fly Ash at Hammond 4, as a Function of Boiler Load (Ref. 12)

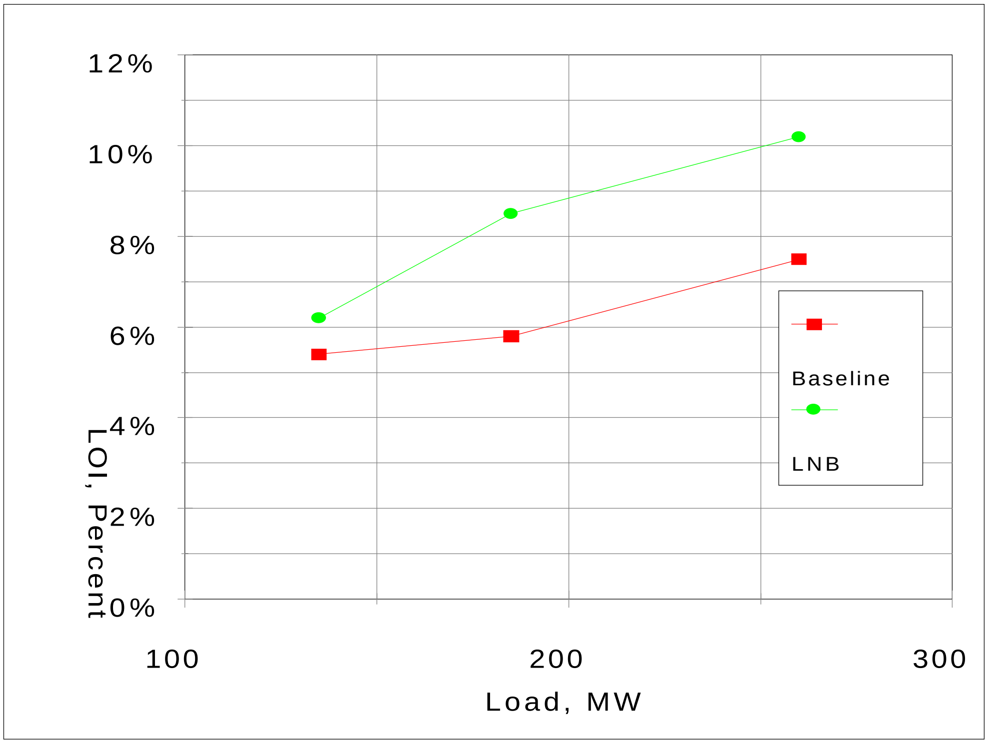

Figure 4-2 Effect of LNB on LOI at Gaston 2, as a Function of Boiler Load (Ref. 12)

Cherokee 3. Reburning technology in conjunction with LNB was demonstrated at PSCC′s Cherokee Station on a 158 MWe wall-fired Unit 3. Initial baseline NO_x emission levels were 0.75 lb/MMBtu with UBC of ~4.0% at full load. Retrofit of LNB resulted in a NO_x reduction of ~40% with an increase in ash carbon levels to 6 percent. The addition of the gas reburning technology on the same boiler resulted in further reduction of NO_x emissions to 65% below the baseline value, while at the same time reducing UBC in the fly ash to 4.5 percent.

Tangential-Fired Boilers

In the USA, at Gulf Power′s DOE Clean Coal Technology demonstration project at Plant Smith (180 MWe Unit 2) burning eastern bituminous coal and demonstrating all three versions of LNCFS (low-NO_x concentric firing systems), no significant changes in UBC were observed when compared with conventional firing.[10,18] One observation made at Smith 2 confirmed the experience of some European utilities, i.e., the positive effect of finer coal grinding on UBC. By improving the coal grind from 65% to 83% through a 200-mesh screen, LOI was reduced by half (from 10% to 5%). At the same time, there was only a small effect on NO_x emission levels. This corresponds well with German experience.[1,5]

Another example of the positive experience with a properly maintained coal mill and the resulting improved coal fineness is that of Potomac Electric Power which indicates that keeping the mill in top condition just by itself can drop the LOI by about 4 percent.[19]

PSCC Cherokee 4 and Valmont 5. Two tangential-fired PSCC boilers at Cherokee 4 (350 MWe) and Valmont 5 (165 MWe) were retrofitted with LNCFS in 1990.[20] The Valmont unit had a history of UBC in fly ash below 2 percent. Comparison of post-retrofit against baseline data for carbon carryover at various loads was very positive (UBC ranged from 1 to 1.5%). At Cherokee 4, slagging problems initially occurred, and although the coal source did not change, a decrease in the ash fusion temperature of 150EC and an increase in the ash content was noted. No information was given regarding UBC levels in the Cherokee 4 fly ash.

East Kentucky Power Cooperative Study. When EKPC John Sherman Cooper Power Station Unit 1 (116 MWe) was converted during the winter of 1993/94, the East Kentucky Power Cooperative jointly with the University of Kentucky Center for Applied Energy Research (CAER) had an opportunity to study and evaluate closely the impact of LNB conversion on the composition and nature of the fly ash.[21,22] For fly ash collection, both mechanical cyclone collectors and a three-field electrostatic precipitator were used, collecting approximately 60%, 32%, 6.5%, and 1.5% of the fly ash, respectively. Fly ash material from each collection bin, as well as the coal feed and the output from the pulverizers were sampled before the conversion, and after the retrofit. Once the whole system was fully stabilized, the same sampling was repeated.

Particle size distribution analysis for both the ash and the organic carbon present, LOI, and elemental composition analysis was conducted on the ash samples. The average particle size of the fly ash decreased following the conversion. Total carbon, in agreement with other similar retrofits, was found to increase by a factor of about two. However, this increase was not uniform over the collection train. The average carbon in the cyclone samples increased from 4.9% before the retrofit to 9.5% after. The ESP carbon increased from 3.3% to 6.3%, representing a 92% increase. However, when only the first ESP field (which produces the bulk of the ESP fly ash) was considered, the increase in carbon was only 65 percent. The increase in UBC was found across every particle size determined, and was not a factor of coal or grinding. The overall carbon concentration in the ash, weighted by mass, increased by a factor of 1.7.

Even though there was no change in the top particle size, as essentially all of the ash passed a 100 mesh (150 mm) screen, the fly ash after conversion was slightly coarser. This was primarily due to an increase in the +150 mm size particles in the dust collectors, this fraction, for example, increasing in one dust collector from 11.6% to 19.8 percent. This increase in size was entirely in the carbon-rich fraction. There was essentially no change in size in the ash collected in the ESPs. The impact of burner conversion on the elemental distribution was not readily apparent from the results.

European Experience

It is noted that a dramatic increase of full-scale retrofit of combustion modifications has been recorded in the European Community countries over the last 15–20 years, reaching approximately 150,000 MWe capacity in 1992.

The report by IEA Coal Research[5] indicates that European experience is similar to that in the USA, as is evident in the following quotation: "Potential impacts of combustion modifications include reduced combustion efficiency; combustion conditions that reduce NO_x formation, such as low combustion temperature and low excess air, are not favorable for accomplishing complete combustion. As a result of this the level of UBC in the fly ash will increase. If this is not counteracted the high content of UBC can cause changed conditions for particulate collection in an ESP and make the fly ash unsaleable. Changes may also occur in the characteristics of fly ash due to reduced combustion temperature. This will make the fly ash less glassy, changing its properties and making the fly ash less attractive for use in cement and concrete production."

Germany

VEBA. VEBA[23] has generally concluded that fly ash quality is affected by combustion NO_x controls, especially the conversion of coal fired boilers to modern types of LNB that reduce NO_x formation by lowering the temperature of the primary flame in the vicinity of the burner tip and cut down the supply of O_2 in the reaction zone. The type of LNBs that have been installed on nearly all German utility boilers, with appropriate inter-adjustments of fuel and combustion, have had minimal effect on the use of coal fly ash as a concrete additive.

VGB. The VGB (German Technical Association of the Power Plants Operators) has stated that the lower flame temperature in furnaces equipped with LNB and the resulting increase in LOI in the fly ash could be compensated for by an increase in the fineness of the coal. Supposedly, the requirement of 5% LOI on fly ash to be used as an addition to concrete or cement can be met in all German power stations. However, it is noted that due to the lower furnace temperature the shape of the fly ash particles is less spherical. As a result of this, the water requirement is increased and the positive effect of fly ash on the workability is less marked. Nevertheless, VGB stresses that combustion NO_x control fly ash is today accepted by the cement and concrete industries in Germany.[24]

ECE NO_x Task Force

Tangential-Fired Boilers. Some other sources, such as the ECE NO_x Task Force report, are less positive about the impact of LNB and OFA on the quality of fly ash. Two Dutch power stations (both using tangential-fired boilers and hard coal)CPZEM Borssele Unit 12 (427 MWe) and EZH Maasvlakte Units 1 and 2 (600 MWe each)Chave had problems meeting the specifications of 5% maximum of unburned carbon in fly ash.[1] It was also noted that the morphology of the ash is different compared to conventional tangential-fired boiler ash. The ash also contains less fine particles (<10 mm). Particles are more agglomerated and more porous. This makes high-grade applications for ash in cement and concrete impossible as the water/cement ratio becomes too unfavorable. Only low-grade applications, for example as raw material for cement clinker production and synthetic aggregates, are possible.

Wall-Fired Boilers. When discussing operating experience with hard coal wall-fired boilers, the same ECE report[1] notes only that the use of very fine coal, obtained through modification of the pulverizers and classifiers, helps counteract the problem of high UBC in fly ash that may occur when using LNB and OFA. Other sources[5] confirm the feasibility of maintaining <5% UBC in fly ash at the guaranteed or expected level of NO_x concentration in the flue gas set at 800 mg/m^3 at 6% O_2, and also mention the increased coal fineness as a measure used at several German plants to counteract the problem of high UBC content in fly ash.

Boilers Fired with Lignite. The ECE report[1] notes that due to the favorable conditions of lignite (i.e., high water content and low nitrogen content) towards low-NO_x formation, and the need for large furnace sizes, which gives low specific heat release and low combustion temperatures, no problems regarding LOI have been observed as yet.

UNIPEDE Report (Belgium, Denmark, Netherlands)

Similarly to other studies and reports addressing the impact of combustion modifications on fly ash, the UNIPEDE (Union Internationale des Producteurs et Distributeurs d′Energie Electrique) report[25] concluded that while the application of combustion modifications can lead to increased UBC in fly ash, there is evidence that in advanced low-NO_x combustion processes the amount of UBC in ash may be limited to values below 5%, mainly through implementation of improved coal milling. At the same time, it is noted that the reduction of flame and furnace temperatures will change the morphology, grain size and shape of the fly ash particles. It was also mentioned that particles with a porous structure have been identified. This report surveys practical experience obtained in a number of European countries, including Belgium, Denmark and the Netherlands, concentrating on the consequences for fly ash quality.

Belgian Power Stations. The UNIPEDE report[25] also provided some typical data from combustion modifications demonstrations and commercial installations in a number of utilities. Typical results obtained in Belgian power stations are given in Table 4-3. The results indicate that primary measures retrofitted on existing stations can reduce NO_x emissions to some extent; however, the increase in UBC, without counteracting measures, was not considered to be acceptable.

Table 4-3
Results of Combustion Modifications in Belgian Power Stations

			NO_x (mg/Nm^3)		UBC (%)	
Unit	**Coal**	**Test**	**Before**	**After**	**Before**	**After**
Langerbrugge 19	S.A.	LEA (02: 3.3–2.8%)	1,075	835	3	6
Langerlo 1	Chinese	OFA	1,300	1,200	3	7
	Austr.	Staged combustion	1,300	1,060	3	7
	S.A.	LEA	1,300	1,000	3	9
Verbrande Brug 2	S.A.	LEA (02: 4.5–3.5%)	1,100	950	2.5	5

Source: Reference 25.

Asnaes, Unit 4. Positive experience has been reported from the Asnaes Unit 4 wall-fired boiler (285 MWe) in Denmark, that was retrofitted with 24 coal/oil LNBs in 1989. As a result, NO_x emissions were reduced from an average of 1260 mg/Nm^3 at 6% O_2 for different types of coals (Polish, American, Canadian, Columbian) to an average of 590 mg/Nm^3. UBC in fly ash was measured daily. The measurements showed no difference with UBC in fly ash from a twin boiler at the same power station. All the measurements showed UBC <5%, and the fly ash was acceptable for use in the cement and concrete industries, meeting the specifications.[25,26]

Maas Power Station, Unit 5. Another low-NO_x combustion installation reported in the UNIPEDE report[25] and elsewhere[27] that sheds some more light on fly ash utilization is the Maas power station, Unit 5. This has been one of the few cases, where particular attention was given to fly ash quality as a consequence of low-NO_x control, and particularly its use in concrete. The Dutch are one of the world leaders in fly ash utilization which have been approaching 100% for years, and in 1989 fly ash utilization for the first time was higher than its production (Table 4-4).

The Maas Power Station has been a demonstration project for a wall-fired 177 MWe boiler retrofitted with sixteen LNBs and eight after air ports. Typical after-retrofit results for NO_x concentration and UBC for four different coals are shown in Table 4-5.

Table 4-4
Production and Utilization of Fly Ash in the Netherlands (in Metric tons)

	1986	**1987**	**1988**	**1989**	**1990**
Fly Ash Production	513,500	613,700	712,400	766,535	850,000 est
Fly Ash Utilization					--
Cement Industry	319,900	369,300	409,300	608,125	--
Asphalt Filler	46,000	43,200	78,500	72,700	--
Artificial Lightweight Mineral Aggregate	84,000	110,400	126,900	121,465	--
Filler in Concrete	27,400	30,400	31,800	28,860	--
Road Constructions/Embankment	18,300	29,000	38,200	150,430	--
Other Applications	7,500	3,400	11,700	1,610	--
Total Utilization	499,000	589,800	696,400	983,190	--

Source: Reference [28.]

Table 4-5
Typical Results for Maas Station Wall-Fired Unit 5

Coal Source/Type		Cerrejon	Illawara	ANR	Drayton
Volatile matter	%	33.0	19.1	31.8	30.3
Ash Content	%	5.4	16.6	7.7	11.0
Fuel volatility FC/VM	--	1.5	3.1	1.7	2.8
LHV	MJ/kg	26.3	26.9	28.5	25.0
NO_x Concentration @ 6% O_2	mg/m^3	480	600	510	430
UBC in fly ash	%	4	4	1.5	1.4

Source: Reference 25.

At the Maas demonstration it was fully realized that low-NO_x combustion controls have an influence on the quality of the ash produced, and consequently, that existing applications could be negatively affected. Despite the fact that fly ash UBC is well within usual specifications (unfortunately, no comparative data regarding UBC before the conversion are given), during the demonstration tests fly ash samples were collected and analyzed for parameters indicative of their applicability for use in construction materials (Table 4-6).

The results of the particle size analysis indicated a slightly more coarse grained fly ash after conversion. However, a comparison with measurements conducted before the project was started, showed the grain distribution hardly differed from that of older fly ashes from the boiler.

The UBC percentage in the fly ash resulting from two-stage combustion was indeed often higher than the guaranteed value of 2.6%, but was still well below 5%, which is the maximum value (in the Netherlands) for utilization in cement or concrete production. The specific surface area was slightly higher after conversion; in view of the small amounts of fine fraction, this has to be attributed to the more porous nature of the ash. The bulk density was lower than that of the samples from March and May 1988 (before retrofit), but it was in the range of the fly ash samples that were obtained earlier.

Table 4-6
Maas Station Fly Ash Quality, Before and After Low-NOx Combustion Retrofit

Parameter	**Before Conversion**		**| After Conversion**			
Date	**3/1988**	**5/1988**	**4/1989**	**5/1989**	**6/1989**	**6/1989**
Coal Source/Type	Cerrejon	ANR	Cerrejon*	Cerrejon	Illawara**	
Particle Size Distribution						
% <10 mm	40	41	39	34	21	21
% <32 mm	87	86	76	74	70	68
% <63 mm	93	93	93	92	92	89
UBC in Fly Ash, %	--	6.6	3.7	2.9	1.9	--
Pozzolanicity, mg SiO_2	11	12	12	10	12	12
Specific Surface Area, m^2/g	1.3	1.1	1.4	1.5	1.4	1.4
Bulk Density, kg/m	1410	1340	1150	990	1190	860
Bitumen Value	35	32	37	36	47	45
Vicat/Water-Cement Factor	0.245	0.246	0.236	0.259	0.283	0.250
Hägermann Value	197	191	169	163	158	181
7d Compressive Strength, N/mm^2	27.0	24.4	27.4	26.3	25.1	27.0
% Against Reference	--	38	80	73	79	--
28d Compressive Strength, N/mm^2	44.2	42.6	36.4	37.8	37.8	39.8
% Against Reference	--	88	91	81	87	--

*Conventional firing
**Two-stage firing.
Source: Reference 25.

For utilization in concrete the results of Vicat, Hägermann value and compressive strength were significant. The water requirement for normal consistency (Vicat) of the fly ash was slightly higher after conversion. The Hägermann values appeared rather unfavorable, but this was not expressed in the results of the compressive strength measurements. These are all in compliance with the requirements of >70% against the reference for seven-day compressive strength and >80% against the reference for the 28-day compressive strength.

The UNIPEDE report concluded that the fly ash from the Maas Power Station demonstration, although its quality deteriorated in some respects after the conversion, was nevertheless suitable for utilization in cement and concrete production. It is stated that: "...all the investigated fly ashes met the standards for industrial applications.”

The retrofit of tangential-fired boilers at the Borssele and Maasvlakte Power Stations in the Netherlands was already noted in the ECE report discussions[1] earlier. The UNIPEDE report as well as a paper by KEMA[29] provide more detailed information, especially regarding the impact on fly ash utilization.

Borssele Power Station, Unit 12. OFA was installed at this 402-MWe facility. It was also mentioned that in order to reduce NO_x concentrations by 20% and to reduce UBC in fly ash below 5%, the coal mills were to be converted and retrofitted with vane wheels and rotating classifiers. Typical after retrofit results for NO_x concentration and UBC for three different coals are shown in Table 4-7.

Table 4-7
Typical Results for Borssele Station Tangential-Fired Unit 12

Coal Source/Type		**McCall**	**Hunter Valley**	**Datong**
Volatile Matter	%	25.6	30.3	29.4
Ash Content	%	13.1	9.8	9.2
Fuel Volatility FC / VM	--	2.0	1.6	1.7
LHV	MJ / kg	25.5	25.8	25.2
NO_x Concentration @ 6% O_2	mg / m^3	624	623	630
UBC in Fly Ash	%	2.4 - 5.9	4.2 - 8.9	5.0 - 10.9

Source: Reference 25.

The UBC of the fly ash increased with increasing amounts of OFA for both the base load and reduced loads. Increasing the tilt of the OFA ports also had a negative effect on LOI. By means of an optical particle size analyzer, the particle size distribution of the fly ash samples was determined. This was done at full and part loads and for different amounts of OFA. Scanning electron-microscope (SEM) analyses were also carried out. A tendency towards an increasing particle size for higher OFA levels was indicated:

		Lower OFA	**Higher OFA**
Full load	d_{50}	18.5 :	22.5 :
	d_{90}	72.1 :	87.6 :
Part load	d_{50}	20.1 :	21.8 :
	d_{90}	71.6 :	77.0 :

where, d_{50} = 50 mass % of the particles smaller than the stated diameter, and d_{90} = 90 mass % of the particles smaller than the stated diameter.[25]

No clear difference could be seen from the SEM photographs. In all eight samples, including those used in experiments with little OFA, not only “normal" fly ash particles were found, but also irregularly shaped porous fragments which looked like "Swiss cheese." Apart from aluminum, silicon, calcium, iron, and thallium, these fragments contained a considerable amount of carbon.[25]

In their papers, KEMA[28,29] have proposed to use an empirical formula, based on Mitsubishi heavy industry formulas, to calculate the LOI from the coal characteristics. MHI uses two formulas:

MHI 2: $\%C = 10F^2 / \text{ash}$
MHI 3: $\%C = 10258\ FC / Cl \times \text{ash}$

where, F = fuel ratio, ash = ash content in dry coal, FC = fixed carbon content, and Cl = combustibility index defined as Cl = HHV x 115 ash / 105 x F.

KEMA have proposed to use the sum of the two MHI formulas to estimate LOI in the fly ash. However, there appears to be considerable scatter in the data.[29]

Maasvlakte Power Station, Unit 2. This tangential-fired boiler (518 MWe capacity) with OFA and increased furnace volume and burner box is similar to Borssele. High volatile bituminous coals, comparable to those used in Borssele were used, usually burnt in blends. Typical NO_x concentrations and UBC for 38 coal blends burnt consecutively varied from 380 to 600 mg/m^3 for NO_x and 3.5 to 12% UBC.[25]

Very few of the coal mixtures fired met the <5% specifications for UBC. Other changes in the characteristics of the fly ash were also observed. SEM microphotographs showed that virtually all samples contain particles of an extremely porous structure, resembling in appearance the particles found in the Borssele P.S. Unit 12. Again, the presence of carbon could be clearly shown in these porous particles.

Bitumen values ranged between 38 and 50, but were mostly around 45, especially for the later fired blends. For the first fifteen coal mixtures, the bulk density of the fly ash was determined. Apart from a single exception, this was always between 660 and 740 kg/m^3. Australian Bloomfield coal produced an extremely lightweight ash (410 kg/m^3), which led to problems in transport and storage of the fly ash. (This is similar to the experience reported by AEP[6] discussed earlier.) In this case this phenomenon was explained by the exceptionally high silicon content in the ash of this coal.[25] KEMA has stressed the importance of keeping the SiO_2/Al_2O_3 ratio below 1.6 to guarantee application of fly ash in the cement industry.[29]

Britain and Italy

British experience on combustion NO_x control have been reported for retrofits at National Power′s Drax 6 and Eggborough 2, and PowerGen′s Cottam 4 stations.[4,30,31,32] All of these are wall-fired units with LNBs installed, burning UK bituminous coal. It was reported that LOI increased from 2–3% to 5% at Eggborough 2, and by 1–2% at Drax 6. Discussing three years of operating experience with LNB in Eggborough, it was noted that: An increase in carbon in dust levels has been observed dependent on the level of excess air employed and NO_x reduction sought".[31] Table 4-8 summarizes their experience.

The trade-off in NO_x emissions and LOI as experienced at the Drax and Eggborough Power Station (and also Hammond 4 unit in the U.S.) is shown in Figure 4-3. A series of burner optimization trials demonstrated how NO_x and UBC can be optimized for Drax 6 situation by adjustment of burner settings. Early LOI increases were also reported at the Cottam 4 unit; however, it was claimed that this has since been resolved. Only one tangential-fired boiler retrofit at PowerGen′s Fiddlers Ferry Station was noted in these early reports, but no effect on LOI was mentioned.

Table 4-8
LNB Experience in NP's Eggborough Power Station

	NO_x Emissions (ppm)	% Carbon in Fly Ash
Pre - LNB retrofit	600–800	1–3
Post - LNB retrofit	400–450	3–8

Source: Reference 31.

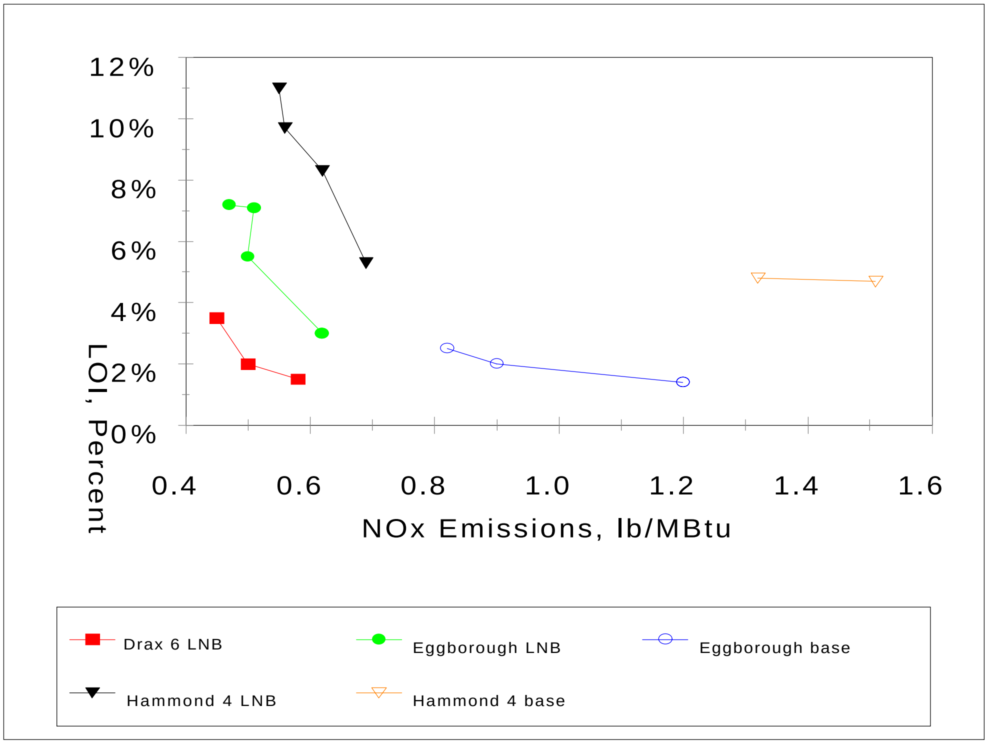

Figure 4-3 Trade-Off in NO_x Emissions and LOI in Wall-Fired Boilers (Ref. 4)

Early experience in Italy appears to be very similar to that in Britain.[4,33,34] Data have been reported for the retrofit of the tangential-fired boiler at Fusina 2 with CCTFS (clustered concentric tangential firing system) incorporating closed-coupled and separated OFA. A significant increase (7 to 10%) in the LOI, which was strongly dependent on the type of coal used, even when ground to high fineness (86–87% through 200 mesh), was observed. Fineness above 90% was required to obtain LOI in the 5-8% range. Table 4-9 presents coal data. Figure 4-4 plots LOI versus firing zone stoichiometry.

A paper that directly addresses British experience regarding the impact of LNB on the quality of fly ash, by comparing fly ashes from ordinary and low-NO_x burners, was co-authored by BRE and National Power scientists.[35] Fly ashes from two power stations were compared, and the properties considered included: mineralogy, glass content, particle size and shape, surface area, pozzolanic index, water demand, LOI, properties of fresh concrete, and concrete strength development (Table 4-10). Material from the power stations is designated A and B, respectively, with samples from low-NO_x units bearing the letter suffix "L". Results are shown in Table 4-10.

Table 4-9
Coals Used in Fusina 2

Coal	**Source**	**Heating Value (Btu)**	**Fixed Carbon (%)**	**Volatility(%)**	**FC/VM**	**Ash(%)**
TCOA	S. Africa	10,911	55.5	21.8	2.6	14.5
AM Coal	S. Africa	11.844	52.8	24.6	2.1	15.1
McCall	US Eastern Bituminous	14,170	64.5	27.8	2.3	6.4
Arch Mineral	US Eastern Bituminous	12,731	50.4	34.4	1.5	7.7

Source: References 4 and 33.

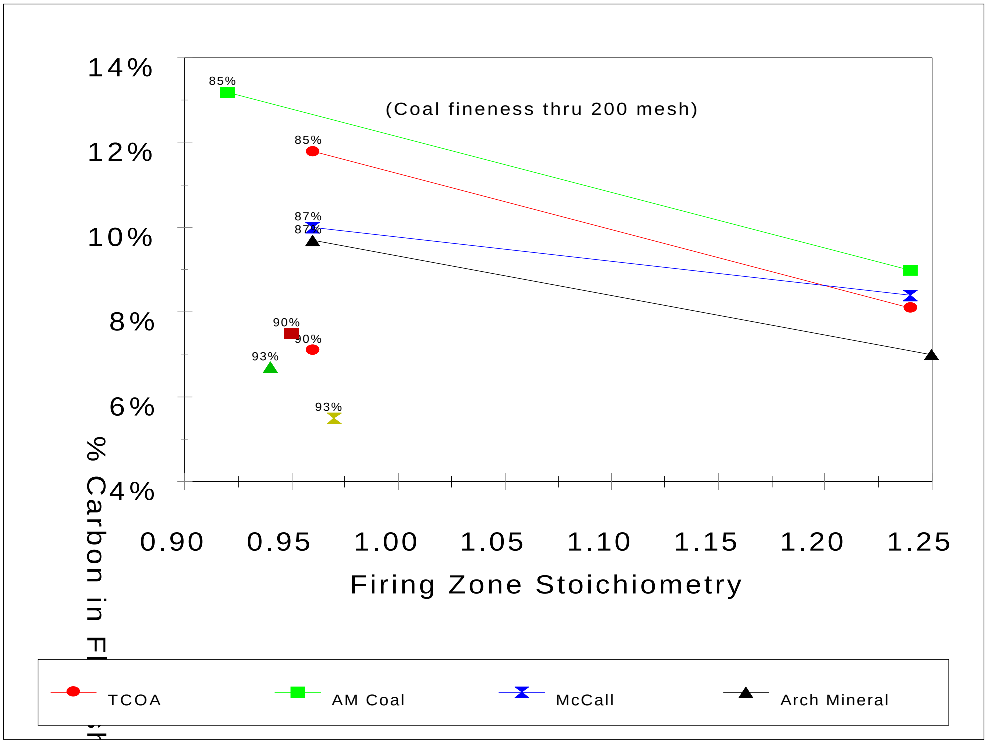

Figure 4-4 Effect of OFA on LOI Levels, Fusina 2 Tangential-Fired Boiler (Ref. 33)

Table 4-10
Characteristics of Fly Ashes from the BRE / National Power Study

Sample	Glass Content	Circularity		Specific Surface	45 mm Sieve	Water Demand	Pozz. Index	LOI
	(%)	Mean	S.D.	Area(m^2/g	Retained (%)	(%)	(%)	(%)
A1	88	1.30	0.38	0.369	7.2	92	96	1.9
A3	88	1.28	0.31	0.424	6.4	94	98	2.9
A2L	86	1.29	0.38	0.309	7.8	90	101	5.1
A4L	84	1.33	0.38	0.322	10.7	94	114	3.9
B2	88	1.32	0.39	0.160	47	89	65	2.9
B6L	80	1.43	0.47	0.331	21	90	81	4.5

Source: Reference 35.

The only significant differences in the chemical composition of the ordinary and LNB fly ashes were in unburned carbon, as indicated by LOI results. The low-NO_x units from both stations produced fly ashes with higher LOI. There was no noticeable difference in mineralogy between the samples, irrespective of the type of burner, the principal crystalline phases being mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), hematite (Fe_2O_3) and magnetite (Fe_3O_4). The calculated glass content for the fly ashes from the LNBs are reduced compared with the normal burners. This does not come as a surprise, as glass formation is dependent on the maximum temperature attained. If the maximum temperature is lowered, all other factors remaining constant, glass formation will be reduced and there will be a corresponding increase in the crystalline fraction. This is consistent with the lower flame temperatures of the LNBs.

With respect to particle shape, no significant differences were noticed for fly ashes from power station A. However, fly ash from the LNB unit of Station–had a significantly higher circularity value, indicating that the particles were less spherical, compared with the fly ash from the baseline unit. The fly ashes from the LNB units at Station A were coarser than the ordinary ashes; however, the situation was reversed for the material from Station B. Rather surprisingly, and contrary to some other reported observations, the results from the water demand tests did not indicate that the burner conditions had any effect. All fly ashes from Station A had similar pozzolanic indices, meeting the BS requirements of 85% minimum. While the pozzolanic indices of the materials from

Station–were below the BS suggested limit, the fly ash from the LNB had a markedly higher index than the fly ash from the ordinary burner.

The concrete mixes were prepared using the following mix design:

- Portland cement: 280 kg / m^3;
- Fly ash: 120 kg / m^3;
- Coarse aggregate: 1,290 kg / m^3; and
- Fine aggregate: 555 kg / m^3.

The water content was adjusted to produce mixes with a slump in the 30–60 mm range. Cubes cast from each concrete mixture were cured in water at 20EC and tested for compressive strength after 7, 28, 56 and 90 days as shown in Table 4-11.

Table 4-11
Characteristics of Fly Ashes from the BRE / National Power Study

Sample	Slump (mm)	W/C +F Ratio	Compressive strength (MN/m^2)			
			7 days	**28 days**	**56 days**	**90 days**
A1	45	0.38	31.0	46.0	50.5	53.6
A3	40	0.38	33.0	48.5	51.0	51.1
A2L	40	0.39	30.0	43.0	48.0	55.4
A4L	40	0.40	30.0	44.0	48.5	49.7
B2	35	0.39	27.0	36.0	41.0	42.4
B6L	50	0.39	24.5	34.0	40.0	41.2

Source: Reference 35.

There were no significant differences observed in compressive strength development for LNB versus ordinary burner ashes at either of the two stations. The authors concluded that although they observed some differences between the low-NO_x and ordinary ashes, the use of LNB ashes did not significantly affect the properties of fresh or hardened concrete. They were of the opinion that the differences in the characteristics of fly ashes due to the burner type were small and generally within the expected range of variation for fly ash from a given power station. It was felt that the suitability of fly ash for use as a cementitious material in concrete was unlikely to be affected by burner type.

Summary

The impact of combustion NO_x control on quality and the continuing utilization potential of fly ash is very site-, equipment- and coal-specific. The main negative effect of NO_x control measures is an increase in the unburned carbon content of the ash. Although in some cases the increase in UBC is small, many utilities experience increases as large as a factor of 2–2.5. Some utilities have been successful in mitigating higher UBC by improved fineness of the coal grind.

Further changes in the character and properties of the fly ash due to combustion modifications include changes in the surface area, higher porosity, elongated, less spherical shape of the ash particles, and a decrease in glass fraction content. Other changes are found in the nature of the carbon itself, which can appear coarse and coke-like or extremely fine and lacy. All these changes in the ash are poorly documented in the literature as is the effect on the inherent reactivity of the material. In general, there is very little currently known about how these characteristics of fly ash are affected by the different types of NO_x reduction technology.

Changes in the UBC and particle properties of the fly ash can have a profound impact on its utilization in some established markets. In particular, all of the mentioned changes affect the use of fly ash in cement and concrete applications. Increased water demand and reduced workability of concrete are among the problem areas directly related to the impact of combustion NO_x controls on the fly ash. The main problem, however, appears to be that UBC in fly ash can prevent the functioning of chemical admixtures such as air entraining agents and, to a lesser degree, of high range water reducers in concrete mixes.

The inability to effectively air entrain concrete with combustion NO_x control affected fly ash is undoubtedly the main concern of the cement and concrete community, as well as of the utility industry. This problem could potentially cause a collapse of this segment of the existing fly ash market in the USA. European experience, however, is somewhat different and not directly transferable to the U.S. While the same effects of LNB and OFA on the quality of the ash have been experienced, it would appear that as long as the UBC can be kept below 5%, such an ash is still accepted by the cement and concrete industry. The fact that, until now, the European cement and concrete industry has not used air entraining agents to any significant degree, however, is of primary importance in continuing acceptance of the low-NO_x fly ash in Europe, as opposed to the U.S.

5

POST-COMBUSTION TECHNOLOGIES

This section provides an examination of the effects that post-combustion NO_x reduction technologies-selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR)-have on ash quality and use. As in the previous section, worldwide sources of information, particularly from Europe, have been reviewed.

Technology Discussion

Selective Catalytic Reduction (SCR)

Selective catalytic reduction (SCR) has been fairly widely applied, especially in California, for both new and retrofit installations, for gas-fired industrial and utility boilers, and combustion turbines. At the present time, it appears to be the most effective commercial technology for stationary source NO_x emission control, albeit usually the most costly one. By this method, high NO_x removal efficiencies-in the 80-90% range depending on temperature, catalyst volume, catalyst deactivation rate and the need to minimize the adverse effects of SO_2 oxidation to SO_3-are achievable. SCR units are usually installed between the economizer and air preheater, although many German systems are located after the FGD and reheat systems.

NH_3 is injected upstream of a catalyst bed, which is located in a 315 to 400°C temperature window. A catalyzed reaction between NH_3 and NO_x takes place to form N_2 and H_2O. Catalysts usually consist of titanium dioxide (TiO_2) as a base material, with the main active component vanadium pentoxide (V_2O_5). Catalysts based on zeolites and activated carbon are used as well. SCR catalysts are supplied either in an extruded honeycomb form or plate configurations. The number of channels per unit, honeycomb pitch and the wall thickness can vary according to the particular SCR configuration and operating requirements.[1]

The optimal temperature range for SCR post-combustion systems, as already noted, is 315 to 400°C. However, SCR technology is evolving. Through further developments, catalyst manufacturers seem to be able to enlarge the applicable temperature window to a wider range (220 to 520°C).[2] The overall chemical reactions can be expressed as:

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{(catalyst)}} 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{\text{(catalyst)}} 3N_2 + 6H_2O$$

U.S. SCR coal-fired applications are very limited. There is significant experience in such installations overseas. The coal sulfur, particulates and volatile heavy metals all pose additional technical feasibility issues for SCR; problems include catalyst poisoning, deactivation and the disposal of the catalyst.

The fuel sulfur content is significant for SCR control technologies, because reactions of SO_2/SO_3 with NH_3 can result in ammonium salt formation on surfaces downstream of the NH_3 injection locations. These reactions can also result in an increase in PM_{10} (<10 µm particulate matter) emissions, if salt condensation occurs outside the stack. The problems of NH_4^+ (ammonium) salt condensation are exacerbated because of the oxidation of SO_2 to SO_3 across the catalyst bed. In addition, sulfur oxides can either poison SCR catalysts directly or as compounds (e.g., alkali sulfates). The fuel particulates/metals content is also an important issue, because these contaminants can cause fouling and poisoning of the catalysts. Newer analyst formulations are believed to be more resistant to these deactivating species.

The commercial applications of SCR systems began overseas in the early 1970s.[3] However, at that time, the technologies developed were used for oil- and gas-fired plants only. The first SCR system on a coal-fired unit started operation at the end of 1980 in Japan. In Europe, the first coal- fired boiler SCR system began operating at the end of 1985 in Germany, followed by further installations in Austria as well as full-scale demonstration plant in the Netherlands and pilot plants in Scandinavia. At the end of 1989, there was a total coal-fired installed capacity of 36 GWe equipped with SCR worldwide with most of plants being in Germany and Japan.[4]

It is important to note that both German and Japanese power plants burn low-sulfur coal (<1.5% S), exclusively. Therefore, the bulk of the world coal-fired utility boiler experience with SCR is not necessarily applicable to the U.S., where medium- and high-sulfur coals are also used.

SCR systems have been developed with the purpose of making the process applicable for different kinds of fuels and boilers. The results of these developments are different SCR configurations, depending on placement position of the catalyst in the flue gas stream:

- High dust arrangement;
- Low dust arrangement; and
- Tail end arrangement.

In the high dust arrangement, the SCR system is located upstream from the electrostatic precipitator (ESP) or fabric filter, and usually upstream of the air preheater (AH). In this configuration, between the economizer and the air preheater, the flue gas temperature is suitable for most types of catalyst. The flue gases passing through the catalyst contain all the fly ash and SO_x from combustion. Therefore, the catalyst must withstand erosion, plugging of pores and outer surfaces, and poisoning due to gaseous trace elements (such as As_4O_6, SiF_4) as well as trace elements in the fly ash, otherwise catalyst degradation will lead to a decrease in NO_x reduction efficiency.[4,5,6] The effect of poisoning by the trace element arsenic has been widely studied, as even very low gaseous arsenic concentrations (~1 µg / m^3) will be captured irreversibly by the catalyst surface.[6]

In a low dust location, SCR is located after a hot gas ESP and before the air preheater. The flue gas reaching the catalyst is almost dust free but contains SO_2. However, hot gas precipitators operating at 300 to 400°C are seldom considered favorably, although they are being installed in Japan, and many older ones are still in operation in the United States.[2]

In the tail end configuration, the SCR system is positioned downstream from the flue gas desulfurization (FGD) unit, at the end of the chain of the flue gas cleaning process.[4,5] The flue gases, therefore, contain only small amounts of SO_x and particulates. The low temperature flue gas has to be reheated to the required catalyst temperature using a heat exchanger. Heat recovery can be provided downstream from the SCR system. The low dust arrangement provides for a smaller volume of catalyst with a prolonged service life due to a relatively clean inlet gas. It is claimed that compared to systems designed for high dust flue gas treatment, catalysts in the tail end region last twice as long, despite their lower catalyst volume.[5]

It is beyond the scope of this study to discuss the relative merits of the three SCR location arrangements. It should be noted that from the point of view of fly ash utilization, the low dust and tail end arrangements have an advantage. Due to the positioning of the SCR unit after the ESP, there is no effect from ammonia slip (see later) on the ash. Nevertheless, based on opera tional factors, the high dust arrangement is preferred and represents about two thirds of the total capacity in the major areas where SCR is installed on coal-fired utility boilers, i.e., in Europe (mainly Germany, 27 GWe capacity), and Japan (8 MWe capacity).[4] The relative merits of the three SCR approaches may be different in the U.S.[7]

Selective Non-Catalytic Reduction (SNCR)

Selective non-catalytic reduction (SNCR) is a control technology that has been successfully applied full-scale (in both new and retrofit installations) to a number of industrial and utility boilers. In SNCR, NH_3, or urea is injected in an optimal temperature window (850°C to 1,100°C) to produce a non-catalytic reaction between NH_2^+ radicals and NO_x. Additional chemicals or enhancers, used in combination with ammonia or urea, can modify the temperature window.

The overall chemical reaction when ammonia is used can be expressed as:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

and when a urea-based process is employed, as:

$$4NO + 2CO(NH_2)_2 + O_2 \rightarrow 4N_2 + 2CO_2 + 4H_2O$$

Ammonia-based SNCR was first developed in the early 1970s by the Exxon Research & Engineering Corporation. It is known as Thermal DeNO$_x$. Between 1976 and 1981, EPRI- sponsored research led to the development of patented urea-based SNCR process, which was licensed, further improved and marketed as the NO$_x$OUT process by Nalco Fuel Tech.

While urea and ammonia offer similar NO$_x$ reduction properties, storage and handling of urea is easier than that of ammonia; also permitting of urea systems has proven to be less difficult.[8] European experience has showed that the investments for storage facilities of urea or aqueous ammonia are about 10-20% of the investments for NH$_3$ storage.[9] Within the SNCR temperature window, urea reacts at slightly higher temperatures (nominally 40°C higher). The combination of urea with various enhancers (e.g., methanol), however, allows tailoring of the process to lower temperatures. Nalco Fuel Tech's basic NO$_x$OUT A system, for example, functions in the 950 to 1,050°C range, while NO$_x$OUT 34, enhanced with a mixture of polyhydric alcohols, lowers the temperature window to about 850°C, and NO$_x$OUT 83 allows operation in the 700 to 850°C window.[10] Of course, the higher cost of enhanced urea reagents has to be taken into the consideration. Additives, such as methane or natural gas, can lower the reaction temperature of ammonia- based SNCR from 850 to 750°C.[9]

A number of other factors can come into the consideration in selection of either ammonia- or urea-based SNCR processes, one of them being the fact that urea produces higher N$_2$O emissions, a significant greenhouse gas. In all the SNCR applications, reagents should be injected at temperatures some 50 to 100°C higher than the respective temperature windows for the mixing and vaporization of aqueous solutions.[11]

For optimal NO$_x$ removal, it is critical that the location of the injection point for the NH$_2^+$ radicals-bearing chemicals is within and perhaps at the high end of the temperature window.

In practice, the reagent decomposition and its reaction with NO$_x$ is expected to be in the convective pass, but it may also occur in the upper furnace.[8] As already noted, temperature is a critical parameter for SNCR, as is the proper configuration of injection points and reagent/flue gas mixing. At higher temperatures, ammonia or urea is oxidized and more NO$_x$ is actually produced; at temperatures below the temperature window, the conversion rate is low and unreacted ammonia will pass through with flue gases[9], being deposited in ESPs on fly ash and leaving through the stack. This is normally called the "ammonia slip." Even under optimal conditions, some injected reagent is not fully consumed in the denitrification reactions, and escapes as ammonia slip. Opinions differ as how the unreacted ammonia is divided between the alternative ways of leaving the plant. However, most of the estimates give the proportion stored in fly ash in the 70-80% range.

As for SCR, ammonia is deposited on fly ash in forms of ammonium salts formed by reactions occurring in NH_3- and SO_3- containing flue gases:

$NH_3 + H_2O + SO_3 \rightarrow NH_4HSO_4$ ammonium bisulfate
$2NH_3 + H_2O + SO_3 \rightarrow (NH_4)_2SO_4$ ammonium sulfate

The ammonium salts will form in the temperature window from 145 to 220°C, with ammonium bisulfate being dominant. Ammonium sulfate, mascagnite, is dry, powdery material. However, ammonium bisulfate is a sticky, partially liquid material which can adhere to surfaces and build up. Deposition will depend on NH_3 and SO_3 concentrations, velocity and temperatures. Deposition of ammonium salts can cause air heater fouling or even pluggage problems, as well as already mentioned fly ash contamination. If ash is sold as a commodity, the absorption of NH_3 may limit its salability. NH_3 absorption by ash may also pose odor and personnel problems in handling the ash.[11]

Issues Affecting Fly Ash Use

Ammonia Slip

NO_x reduction is directly related to the amount of ammonia injected, expressed usually as a molar ratio of NH_3 to NO_x. At a NH_3 to NO_x ratio above 0.90, however, little additional NO_x removal is achieved, whereas the amount of unreacted ammonia in the flue gas, so called "ammonia slip," increases significantly.[8]

Unreacted ammonia will pass through with flue gases[10], with most being deposited, in the preferred high dust SCR configurations, on the fly ash in the ESPs, and the rest leaving through the stack. Even under optimal conditions, some injected reagent is not fully consumed in the denitrification reactions, and escapes as ammonia slip. Opinions differ as to how the unreacted ammonia is divided between the alternative ways of leaving the plant. However, most of the estimates give the proportion retained on fly ash in the 70-80% range. At flue gas temperatures of ~370°C, NH_3 is in a gaseous form. With temperatures of ~140°C at the air heater and in the presence of SO_3, condensation takes place with the simultaneous formation of ammonium sulfates and a rapid decrease in the NH_3 concentration. The condensation products are discharged onto the fly ash and in part onto the air heater; over 80% of the NH_3 slip is therefore transported on the fly ash into the dust precipitator. It has been observed[12] that in the ESP, gaseous NH_3 is subsequently adsorbed on to the fly ash. Given a concentration of 5 ppm in the gaseous phase in front of the ESP, generally no gaseous NH_3 can be detected behind the precipitator.

It is not only the higher NH_3/NO_x ratio (>0.9) that will cause higher, and usually unacceptable ammonia slip. If the ammonia injection system does not provide a uniform distribution in the NH_3 to NO_x molar ratio across the catalyst face, some regions will experience high relative NH_3 concentrations that can lead to higher levels of NH_3 slip.[8] Furthermore, NH_3 slip is not constant over the lifetime of the catalyst. As the catalyst ages, it loses its activity, and the amount of NH_3 slip is increased. The amount of unreacted ammonia in the flue gas is thus a good measurement of the status of the catalyst and the SCR plant. Ammonia slip is used as the criterion for when it is time to add or to replace the catalyst. European plants usually have guaranteed catalyst lifetimes of 12,000-16,000 operating hours (maximum 3-4 years) for installation on dry bottom boilers, and 12,000 operating hours for installations on wet bottom boilers, with an ammonia slip less than 5 ppm at the end of that period.[4,13]

The actual catalyst lifetime is a major issue, as the cost for its replacement dominates the other operating costs of an SCR plant.[4] As already noted, positioning of the catalyst in a high dust versus a low dust or tail end SCR arrangement dramatically affects catalyst life. Also, the "cleaner" the fuel, the longer will be the expected catalyst life. As SCR is a relatively new technology, it is hard to predict catalyst life. However, there is an indication that earlier predictions and guarantees regarding catalyst life were probably on the conservative side. There are indications that the actual performance will be better than the originally expected life. One U.S. SCR catalyst manufacturer offers the estimates shown in Table 5-1.

There is an inherent trade-off between NO_x emissions and ammonia slip in the design of SCR or SNCR systems[8], resulting in ammonia contamination of the ash and NH_3 emissions from the stack.

Table 5-1
Catalyst Life

Fuel	Expected Life	Actual Performance
Gas	3 years	10 years
Oil	2 years	8 years
Coal	2 years	5+ years

Source: Reference 2.

Ammonia is extremely odorous at concentrations as low as 20 ppm in the ash. Contamination has affected ash sales at some locations.[8] The odor threshold for ammonia is 1-5 ppm, and the current recommended 8-hour occupational standard is 25 ppm.[14] A number of investigators have studied the human health effects of acute NH_3 exposure of varying durations and concentrations. In no case has an ammonia concentration less than 30 ppm been found to have adverse health effects on humans.

In addition to the odor, there is also a problem with utilization of fly ash in some processes, particularly for concrete production, when the ammonia content exceeds 50-100 mg NH_3/kg fly ash.[4] Fly ash contains small amounts of ammonia which originates from combustion, on average 10 mg NH_3/kg fly ash. SCR systems are generally designed for ammonia slips of less than 5 ppm in the flue gas. A typical ammonia slip of 2-4 ppm for a newly installed SCR corresponds to 20-50 mg NH_3/kg fly ash. In some cases, experience has shown that with a slip of more than 2 ppm, fly ash cannot be used by the cement industry. This especially applies to hard coal with low ash content (<5-8%) (15). In some operations in Germany, to ensure that ash remains odor-free and salable, the maximum acceptable value for total NH_3 slip is about 1.5-2 ppm.[15]

Ammonia is deposited on fly ash in the forms of solid ammonium compounds, the results of reactions that occur in flue gases containing NH_3 and SO_3:

$NH_3 + H_2O + SO_3 \rightarrow NH_4HSO_4$ ammonium bisulfate

$2NH_3 + H_2O + SO_3 \rightarrow (NH_4)_2SO_4$ ammonium sulfate

The ammonium salts will form in the temperature window 145 to 220°C, with ammonium bisulfate being dominant. Ammonium sulfate is a dry, powdery material. However, ammonium bisulfate is a sticky, partially liquid material which can adhere to surfaces and cause build up. Deposition will depend on the NH_3 and SO_3 concentrations, velocity and temperatures. In reality, it is always a mixture of these two compounds which is formed and deposited.[10] The formation of the ammonium salts depends on the temperature, SO_3 concentration, NH_3 slip and the location of the catalyst in the flue gas stream.[16]

In a boiler with 500 MW electric capacity and about 1.5-million Nm^3 per hour flue gas, 2,000 kg of ammonium sulfates are formed daily, given typical NH_3 and SO_3 concentrations in the flue gas of 10 ppm.[10] Deposition of the ammonium salts can cause air heater fouling or even pluggage problems, as well as the already mentioned fly ash contamination. If ash is sold as a commodity, the absorption of NH_3 may limit its salability. NH_3 absorption by the ash may also pose odor and personnel problems in handling the ash.[11]

Potential Fly Ash Problems in SCR Systems

It is widely recognized that precipitation of ammonium salts on the fly ash can have significant impact on waste disposal or marketing practices. In the case of an Eastern coal with acidic constituents, off gassing of ammonia from ash will not likely occur during waste disposal. However, ammonium bisulfate will off gas ammonia when the pH is raised, and as a result the fly ash may not be a marketable commodity to the construction industry. Reuse options may be limited. Direct use of such ash as an admixture in cement manufacturing may be jeopardized if the NH_3 content is too high.[17,18] The use of contaminated fly ash in concrete applications would be even more of a problem than in cement manufacturing.

There are different methods and processes available to remove ammonia from fly ash, including thermal reduction and stripping with steam or air (see Section 6 of this report). At this time, there are no such commercial operations in either the USA or Europe. Pilot plants are operating in both Germany and Japan.[4]

Potential Fly Ash Problems in SNCR Systems

It is fully realized by U.S. utilities and EPRI that ammonium bisulfate precipitation on the fly ash can have significant impact on waste disposal or marketing practices. As this issue has received little research attention to date, a bench-scale study to characterize NH_3 absorption by fly was recently conducted.[19] The experiment investigated NH_3 absorption as a function of ash type (four coal ashes, two oil ashes), exposure time, temperature, and NH_3 content. Some of the properties of the fly ash sources used in this ESEERCO-sponsored study are given in Table 5-2. In order to attempt correlations between NH_3 absorption and fly ash characteristics, surface area (BET), sulfate content, pH and carbon content were determined on the ash samples (Table 5-3).

Table 5-2
Fly Ash Sources and Nominal Properties

Utility	Unit	Fuel Type	Fuel Sulfur (%)	Ash Collection
NIMO	Oswego 6	Oil	1.5	Baghouse Hopper
LILCO	Port Jefferson	Oil	1.0	ESP Hopper
NIMO	Huntley	Coal	n/a	N/A
RG&E	Russel 4	Coal	n/a	N/A
NEP	Salem Harbor	Coal	0.7	ESP Hopper
PSCC	Arapahoe 4	Coal	0.5	Baghouse Hopper

Source: Reference 19.

Table 5-3
Fly Ash Characteristics

Ash Source	Fuel Type	Surface Area/BET (m^2/g)	SO_4 (wt %)	pH*	Carbon (%)
Oswego, NIMO	Oil	4.11	33.98	8.6	4.48
Port Jefferson, LILCO	Oil	5.72	24.27	3.4	6.93
Huntley, NIMO	Coal	8.08	0.78	7.7	10.81
Russel, RG&E	Coal	1.23	0.66	9.8	1.17
Salem Harbor, NEP	Coal	15.33	0.49	10.1	37.82
Arapahoe, PSCC	Coal	12.79	0.37	10.0	6.16

*For 0.25 g of ash sample in 200 mL of distilled water.
Source: Reference 19.

The two primary variables during these simulated tests were (1) the contact time between the ash samples and the NH_3 laden flue gas stream, that was varied between two minutes and one hour, and (2) the temperature, ranging between 250 to 325°F, a representative range of utility boiler heater outlet temperatures. The simulated flue gas contained 10 ppm of NH_3. The authors of this study considered this NH_3 slip value as representative of potential regulatory and/or operational limits, although it appears to be 2-5 times higher than what is allowed and practiced overseas. In a single case, the impact of NH_3 slip of 20 ppm on ash was evaluated as well. A summary of NH_3 absorption results at one (intermediate) temperature setting, 300°F, for exposure times of 10 and 60 minutes, is shown in Table 5-4.

Table 5-4
NH_3 Absorption Onto Fly Ash at 10 ppm Slip at 300°F

Ash Type and Source		NH_3 Absorption, (ppmw, 10 minutes)	NH_3 Absorption, (ppmw, 60 minutes)
Oil Ash	Oswego, NIMO	432	1,893
	Port Jefferson, LILCO	467	1,654
Coal Ash	Huntley, NIMO	9	132
	Russel, RG&E	159	190
	Salem Harbor, NEP	166	344
	Arapahoe, PSCC	222	347

Source: Reference 19.

An attempted correlation between NH_3 absorption and several different ash characteristics produced no definitive conclusions, although some light was shed on the issue through the following observations:

- Oil ashes absorb substantially more NH_3 than coal ashes;
- At all temperatures, the amount of NH_3 absorbed by the oil ashes continued to increase linearly with time;
- After one hour of exposure, the absorbed NH_3 levels for the oil ashes varied between 2,000 and 3,000 ppm;
- In contrast, coal ashes absorbed substantially smaller amounts of NH_3 (<500 ppm);
- For coal ashes, most of the absorption occurred in the first 5 to 10 minutes;
- The lowest ammonia absorptions tended to occur at highest temperatures; and
- The only parameter that tends to suggest some correlation between NH_3 absorption and ash characteristics is the sulfate content of the ash.

The authors concluded that additional research is needed to determine what factors govern NH_3 absorption onto fly ashes.

SCR-U.S. Experience

There is currently very limited full-scale experience, and only a limited number of pilot-scale tests, with SCR for the many coals with >2% sulfur currently burned in large quantities in the USA.[8] There are concerns that the European and Japanese experience may not be directly transferable to these U.S. applications due to differences in the coal characteristics.

DOE Clean Coal Technology Demonstration Program

Southern Company Services, Inc. (SCS), is demonstrating SCR technology for the control of NO_x emissions from high-sulfur coal-fired boilers under the DOE Clean Coal Technology Demonstration Program[20,21,22] which is being co-funded by EPRI and Ontario Hydro. The demonstration facility, located at Gulf Power's Plant Crist near Pensacola, FL, consists of three 2.5-MWe-equivalent SCR reactors and six 0.2-MWe-equivalent SCR reactors, supplied by a total of nine flue gas slipstreams. Eight of the nine reactors operate with flue gas containing full particulate loading (high dust) extracted from the inlet duct of the hot-side ESP, while one small reactor uses flue gas fed from the ESP outlet (low dust). These reactors were sized to produce design data that will allow the SCR process to be scaled up to commercial size.

The demonstration plant uses flue gas from the station's 75 MW Unit 5 which burns principally Illinois No. 5 coal with ~3% sulfur under various NO_x and particulate level conditions. Targeted NO_x removal rates are 80%, with slip <2 ppm under baseline conditions. Construction began in March 1992. Commissioning tests without catalysts began in March 1993, and two-year operations phase began in July 1993. Nine different catalysts of various shapes and compositions were provided by three U.S., two European and two Japanese suppliers. Test operations are in progress. The first year's results for NO_x removal and ammonia slip for all catalysts are as good as, or better, than design expectations.[23]

Quality and potential marketability of the fly ash was not a project objective, although its behavior and the way it affects operation and equipment maintenance, of course, is.[22] It is noted, however, that in general, fly ash has not affected the pilot plant; however, the ash characteristics have affected the test and sampling equipment. Studies are under way to determine the interactions between fly ash, ammonia, and ammonium-sulfur compounds, particularly around the air preheaters. The final report on this demonstration project is expected by October 1995.

EPRI Sponsored TVA and NYSEG Pilot Projects

EPRI has been involved in additional SCR pilot projects on coal-fired boilers, namely at TVA's Shawnee and NYSEG's Kintigh power stations.[24,25,26,27] TVA's Shawnee plant uses 4% sulfur coal, and the high-dust SCR pilot here represents the world highest sulfur SCR installation; NYSEG's Kintigh plant is a tail end, post-FGD SCR system. While fly ash tolerance for NH_3, SO_3 and byproducts is one of the stated key questions addressed in the pilot trials, no data on NH_3 content in fly ash are reported for inclusion in this report.

Merrimack Power Station, PSNH

In 1995, Public Service of New Hampshire installed a SCR system at its Merrimack, NH station. This retrofit of Noell's SCR reactor on an existing cyclone boiler is to be the first commercial installation of SCR technology on coal-fired utility in the U.S. It is to be commissioned by mid- 1995.[28]

Orlando Utilities Commission, Stanton Unit 2

Orlando Utilities Commission's 460 MW Stanton 2 Unit will require post-combustion treatment to meet NO_x emissions permit requirements. From reports of the selection process for the NO_x emissions treatment plant,[29] it is evident that some emphasis has been put on fly ash quality and marketability. Based on technology screening, three NO_x emission reduction alternatives were considered technically viable:

- An SCR system designed for a maximum outlet NH_3 slip of 2 ppm, resulting in no loss of fly ash sales, and the lowest potential impact on plant availability.

- An SCR system designed for a maximum outlet NH_3 slip of 5 ppm resulting in a 50% loss of fly ash sales, and relatively moderate potential impact on plant availability.
- An SNCR system designed to meet a NO_x outlet emission of 0.17 lb / MBtu. Ammonia slip emissions would result in a total loss of fly ash sales, and the largest potential impact on plant availability.

OUC had concerns about the NH_3 level in the fly ash and the impact it could have on waste disposal and marketing practices, being aware that at elevated pH, ammonia in the fly ash will be released, possibly leading to odorous emissions. While eastern U.S. coals are not inherently alkaline, fixation of fly ash with alkaline species from a wet limestone scrubber, or when used as part of raw meal in cement manufacturing or as an admixture in other pozzolanic uses, will result in ammonia releases. Citing German experience, OUC believes that fly ash NH_3 concentrations greater than 100 mg / kg (100 ppm) result in noticeable odor and may result in rejection by the cement industry. Testing has indicated that for coal with 7% ash, NH_3 slip must be limited to below ~2 ppm to avoid potential problems.

It was concluded that while a typical SCR system guarantee would be a maximum 5 ppm NH_3 slip for a catalyst life of two years, with the addition of ~20% more catalyst to the initial charge, catalyst suppliers would be willing to provide a guarantee of 2 ppm NH_3 slip for a catalyst life of two years. On the other hand, SNCR system suppliers currently guarantee NH_3 slip levels of 10 ppm only in an optimized steam generator. Given the existing equipment design, and the levels of performance necessary at the Stanton Unit 2, it was concluded that an NH_3 slip of 10-50 ppm would be likely. Accordingly, it is expected that all fly ash sales from Unit 2 and the opportunity for scrubber solids fixation with Unit 2 ash would be lost.

It was concluded on the basis of detailed technical and economic analysis that the selection of an SCR system with a 2 ppm NH_3 slip rate is the preferred option for Stanton Unit 2. Such a system, allowing full fly ash marketability and utilization, has the lowest evaluated levelized annual costs, despite the higher capital costs. The SCR plant at Stanton Unit 2 is to come on stream in 1996.

SCR-European Experience

In increasing numbers of power stations, secondary control measures are applied to meet strict NO_x standards. SCR is a dominant post-combustion technology used on coal-fired utility boilers in Europe. In 1990, out of 140 such operations, 92% were SCR-based, 7% SNCR-based, with 1% using some other techniques. Considering the capacity of these operations, the numbers favor SCR even more, with 94% of the total capacity employing SCR and only 5% using SNCR processes.[30]

Most of the longer term commercial SCR experience is in Germany and Austria, with a number of boilers being equipped with such systems between 1986 and 1990. Practical experience, as reported in literature, is therefore somewhat limited at this time to the experience in these two countries. Italian utilities were planning a large number of SCR installations in 1992 and later, but no results have been published at this stage.

With an increasing number of European countries actively considering post-combustion measures to reduce NO_x, there are concerns with respect to NH_3 absorption by fly ash. The maximum acceptable concentrations are under discussion[15], the accepted upper value of NH_3 in fly ash being at present 50-100 mg/kg.[10] The consequences for fly ash utilization in relation to the odor threshold value, and the impact of NH_3 on the manufacturing process and quality of the products are under consideration. In Denmark, 200 mg/kg is considered the maximum acceptable limit in SNCR, and one can assume that also in SCR processes.

Germany

Germany has the largest installed capacity of NO_x control measures. The maximum federal legal limit for NO_x concentration in flue gas from coal-fired power plants is 200 mg/m^3 (s.t.p., dry).[13] Of its 46 GWe coal-fired total capacity, 33.7 GWe is fired with hard coal. Although almost all German utility boilers are equipped with combustion operation modifications such as LNB, air staging and operational optimization, for hard coal-fired boilers these measures have not been sufficient to achieve the stringent emission standards. Consequently, most hard coal-fired boilers in Germany (it is not stated explicitly in the literature references, but it is assumed that all of this information concerns former FRG prior to unification) are equipped with both combustion modifications and SCR. At the end of 1989, there were about 100 SCR units (~26-28 GWe) installed on hard coal-fired plants.[13,30] In hard coal-fired plants with dry bottom boilers, the SCR plants are mainly operating as high dust systems. Power plants with wet bottom boilers usually have the SCR plant appended to the FGD system as a tail end process. For most of the brown coal-fired operations (12.3 GWe, or about 27% of the total German capacity), it has been possible to reduce NO_x emissions to the acceptable levels using just combustion modifications. There are only a few SCR equipped brown coal plants in Germany, representing about 0.5 GWe.[30]

The performance of a number of German SCR plants have been reported in the public literature[10,13,31,32,33], including:

- Altbach/Deizisau PS Unit 5: Neckarwerke;
- Walheim PS Unit 2: Neckarwerke;
- Heilbronn 7: Energieversorgung Schwaben AG;
- Knepper Unit 3: Veba Kraftwerke Ruhr AG;

- Schwandorf Unit D: Bayernwerk AG;
- Hafen 2: Hamburgische Electrizitätswerke; and
- Karlsruhe West K3: Stadtwerke Karlsruhe.

Not all reports deal with the effect of their SCR units on the quality of ash. Not surprisingly, NO_x reduction, operation and maintenance of the SCR unit itself (catalyst degradation, ammonia system maintenance) and the effect of the SCR unit on the operating and maintenance of the boiler and downstream equipment (corrosion, ammonia slip, SO_2/SO_3 conversion, fly ash deposits, fouling and blockage) have much higher priority than the potential effects and concerns regarding fly ash quality. Nevertheless, a conclusion is made, stating that:

"The experience shows that with a NH_3 slip of more than 2 ppm fly ash cannot be used by the cement industry anymore. This especially applies for hard coal with low ash content (<5-8%)."[13]

Both Neckarwerke (Altbach/Deizisau and Walheim) plants were demonstration projects for introduction of SCR technology in Germany, they were sponsored by the German Federal Environment Agency (UBA) in Berlin, and the experience gained was well reported and disseminated.[33,34]

Altbach/Deizisau PS Unit 5, Neckarwerke.

Configuration:	SCR at dry bottom boiler (420 MW), high dust location, hard coal
Year of start-up:	12/1985
Accumulated operating hours:	18,400 hours as of 12/1988

A considerable amount of information has been reported for this SCR operation (this being the first large-scale industrial unit built and operated in Germany), including mention of startup problems, ammonia slip, and NH_3 levels in fly ash.[4,31,33] Ammonia in fly ash has proven to be a crucial operating problem in Altbach/Deizisau.

Based on Japanese experience and the recommendations of suppliers, the original order for the SCR plant for Altbach/Deizisau specified an NH_3 slip of 5 ppm (~3.8 mg/m^3). An acceptance of this recommended slip value proved to be an error. Neckarwerke, as many other utilities, has an agreement with a large cement manufacturer that uses fly ash from Altbach/Deizisau. Approximately 22% of ash is added to the cement clinker to produce blended fly ash cement.[31] It was recognized that if the NH_3 concentration in the fly ash exceeds a certain value, this may result in release of NH_3 during concrete mixing due to the alkaline characteristics of the cement, and thus to noticeable odor.

Neckarwerke believes that, depending on the intended purpose and type of use, 100 mg NH_3/kg fly ash is a maximum limit value for the NH_3 concentration, and that for 60 mg NH_3/kg and above, special conditions apply for disposal. If the NH_3 content of the fly ash jeopardizes the utilization of the ash and thus the waste disposal practices of a power plant, it is a serious problem. (It is claimed that while NH_3 release and resulting odor was considered a crucial problem, their own tests have shown that the concrete properties are not altered by these effects.)

Altbach/Deizisau uses relatively high-quality hard coal types with an ash content of 6-8 percent. Initial information from 1984-86 showed that about 70% of the NH_3 slip is absorbed on fly ash. On this basis, it was estimated use of coal with a 7% ash content, an NH_3 slip of 1.4 ppm results in ~100 mg NH_3/kg of ash (a value considered a maximum limit), and an NH_3 slip of 5 ppm, the original specification, results in ~350 mg NH_3/kg of ash.[33]

In ten tests during 1986-88, NH_3 deposits on fly ash were on average about 50% lower than estimated. Careful measurements detected up to 50% leakage in the heated combustion and mill air flow. These results are somewhat incongruous in comparison with earlier measurements and up to 80% absorption reported by others. It would appear that the ratio of NH_3 ash deposition and plant leakage is site and installation specific.

Based on the experience at Altbach/Deizisau Unit 5, Neckarwerke and many other German utilities now design SCR catalytic converters for an ammonia slip of 2 ppm maximum. However, over sizing the catalyst can have the disadvantage of increasing the conversion of SO_2 to SO_3, thereby creating another problem.

Wahlheim PS Unit 2, Neckarwerke.

Configuration:	SCR at wet bottom boiler (150 MW), high dust location, hard coal
Year of start-up:	11/1987
Accumulated operating hours:	7,533 hours as of 12/1988

The design of this unit was based on the experiences gained at the Neckarwerke Altbach/ Deizisau Unit 5. Ammonia slip values due to process optimization and only the first 6,000 hours of operations at the time of the report[33] were rather low, resulting in the NH_3 deposits on the fly ash of only 10 and 20 mg/kg.

ECE NO_x Task Force. The ECE report[10] discussed the operating experience of five SCR-equipped coal-fired boilers shown in Table 5-5. It was decided to show these five operations as representative of the widest possible conditions and options, and consequently not all of them represent typical, or popular SCR installations.

Table 5-5
Matrix of German SCR Installations Reviewed by ECE

Unit / Boiler	Boiler Type	Coal Type	SCR Configuration	Representative of No. of Units
Heilbronn 7	dry bottom	hard	high dust	36
Knepper Unit 3	wet bottom	hard	high dust	15
Schwandorf Unit D	dry bottom	brown	high dust	3
Hafen 2	dry bottom	hard	tail gas	11
Karlsruhe West K3	wet bottom	hard	tail gas	24

Source: Reference 10.

Heilbronn 7-Energieversorgung Schwaben AG.

Configuration:	SCR at dry bottom boiler, high dust location, hard coal
Year of start-up:	11/1986
Mode of operation:	4,700 hours/yr
Accumulated operating hours:	18,400 hours as of 5/1990 25,000 hours as of 3/1991

The inlet NO_x concentration ranges from 650 to 750 mg/m^3. The operating setpoint for the NO_x outlet concentration is 160 mg/m^3 at a maximum. The NH_3/NO_x ratio was 0.8. Initially, the NH_3 slip was as low as 0.5 ppm (0.38 mg/m^3), but measurements in 1989/90 showed an increase up to 1.4 ppm with maximum peak values of 2.2 ppm.[10] This was attributable to an increased fly ash deposition on the catalyst, thus reducing its activity. After 18,400 hours one of the SCR reactors was cleaned and the NH_3 slip was reduced back to 0.5 ppm. The soot blowers of the first catalyst layer had to be used daily as opposed to once a week. An incident of noticeable ammonia odor in the Heilbronn fly ash, at an ammonia slip of less than 5 ppm, when plugging of the catalyst occurred, is reported.[32]

At 12,000 operating hours the ammonia recorded was 30 mg/kg of ash compared to 10 mg/kg at start-up. At about 18,000 hours, measurements showed that the ammonia content increased between part load and full load, whereby the maximum was reached after a 6-hour delay. The longer the number of full load hours, the higher the ammonia content. Peak values of 80 mg/kg were recorded in the winter months of January and February 1990. The daily average dropped to 50 mg/kg in April/May. During part load a limit value of 30 mg/kg was obtained. After cleaning the reactors, the ammonia content in the fly ash was reduced to 20 mg/kg at full load operation. (Before start-up of the SCR plant the NH_3 content in the fly ash ranged between 6 and 15 mg/kg.)

No comments were made regarding any negative effects of fly ash ammonia content on any application. However, in another paper discussing Heilbronn 7, it was noted that as the utility is selling high-quality fly ash, they indeed try to run at very low ammonia slip.[34] As of spring 1991, following 4.5 years of full-scale experience, no problems were experienced.

Knepper Unit 3-Veba Kraftwerke Ruhr AG.

Configuration:	SCR at wet bottom boiler, high dust location, hard coal
Year of start-up:	6/1986 (50%), 8/1988 (100%)
Mode of operation:	6,000 - 8,000 hours/yr
Accumulated operating hours:	~31,000 hours as of 12/1990

The NO_x reduction at Knepper C is required to be >90 percent. In conjunction with the fly ash deposit on the catalyst, the NH_3 content in the fly ash rose to such an extent that the NO_x emissions had to be raised from 200 to 400 mg/m^3. The regular operation of soot blowers (three times a week) has solved the problem

Schwandorf Unit D-Bayernwerk AG.

Configuration:	SCR at dry bottom boiler, high dust location, brown coal
Year of start-up:	6/1988
Mode of operation:	4,000-4,500 hours/yr
Accumulated operating hours:	13,800 hours as of 12/1990

Flue gas treatment is necessary in very few cases in brown coal-fired power plants. Schwandorf appears to be the only such operation in Germany using SCR, although another SCR-equipped brown coal-fired facility was commissioned at Voigtsberg 3, Austria. The SCR reactor was initially designed for an assumed inlet NO_x concentration of 650 mg/m^3 (at 4% O_2), compared to the actual value of 500 mg/m^3. The adjusted outlet NO_x concentration was 130 mg/m^3, which determined the ammonia injection rate. For a given NH_3/NO_x ratio of 0.7, the NH_3 slip was <0.1 mg/m^3.

This operation reports experience opposite to most of the other SCR installations. Here pre-SCR measurements showed that NH_3 concentrations after the air heater were much higher without the SCR process. A natural NH_3 content in the boiler of 20 mg/m^3 and a slip of 1.0-1.5 mg/m^3 were measured. The 90% reduction of this slip is attributed to the SCR catalyst, at which flue gas ammonia can react with NO_x. Consequently, the concentration of NH_3 in fly ash has been reduced from the pre-SCR days, and is reported to be in the 15-30 mg/kg range.

Hafen 2-Hamburgische Electrizitätswerke.

Configuration:	SCR at dry bottom boiler, tail gas location, hard coal
Year of start-up:	9/1987
Mode of operation:	7,500 hours/yr
Accumulated operating hours:	~20,200 hours as of 5/1990

This is a tail gas SCR reactor; consequently, there is no effect on fly ash quality. In the flue gas stream at the stack, the NO_x concentration depends on the leakage at the heat exchanger as well as on the raw gas NO_x concentration, and does not fall below 60-120 mg/m^3 even at maximum NH_3/NO_x ratio. At a NH_3/NO_x ratio = 1, the NH_3 slip rises as high as 6 mg/m^3 or over . The average NO_x reduction rate is between 75-80 percent. (The design value is 79%) The present NH_3 slip is below 1 ppm (about 0.4 ppm).

Karlsruhe West K3-Stadtwerke Karlsruhe.

Configuration:	SCR at wet bottom boiler, tail gas location, hard coal
Year of start-up:	3/1989
Mode of operation:	6,000 - 8,000 hours/yr
Accumulated operating hours:	~12,000 hours as of 3/1991

This is another tail gas SCR configuration, this time on a wet bottom boiler. The NH_3 slip downstream of the FGD system is about 1.5 kg/h (about 8 ppm). This NH_3 is either burnt in the SCR preheating system or further involved in the NO_x reduction in the SCR plant. The total NH_3 slip at the stack is below the design value of 5 ppm. As the SCR plant is located downstream of the ash collection system, there is no effect on the quality of ash. The NO_x reduction rate is greater than 90% at a NH_3/NO_x ratio of almost 1.0.

German Experience-Remarks.

Over 120 large scale SCR plants are operating successfully in Germany and other ECE countries. The SCR plants installed on dry bottom boilers are on average designed for 75-80% NO_x reduction. The guaranteed catalyst lifetimes of 3-4 years have been exceeded in most cases. For high dust locations, up to 5 years have been reached; and for tail gas locations, 10 years are projected. Installations on wet bottom boilers are designed for NO_x reduction of ~90%, and guaranteed catalyst lifetimes 3-4 years for high dust and tail gas configurations, respectively.[10]

The SCR process has been implemented at gas-, oil- and coal-fired installations. The coal compositions are shown in Table 5-6. Up to now, nearly all installations have been retrofits. Experience has shown that most problems as a result of retrofit can be solved. The NO_x inlet concentrations range between 300 mg/m^3 (for gas) and 500 mg/m^3 (for coal) up to 2,200 mg/m^3 (for wet bottom boilers). The SCR technology is appropriate for base, middle and peak loads.

Table 5-6
Range of Characteristics of Coals Used in German Utility Boiler Equipped with SCR Plants

Constituent	**Range (%)**
Ash	5-48
Sulfur	0.8-2.2
Nitrogen	1-2
Chlorine	0.1-0.2
Moisture	8-27

Source: Reference 10.

Ammonia slip, the result of the incomplete reaction of ammonia with NO_x, is always present in SCR systems. Estimates are that for 80% of the guaranteed catalyst lifetime, NH_3 slip will be between 0.5-2 ppm. For the remaining 20% of the time, the slip will increase to 5 ppm (usually the value for which the catalyst is designed) as the catalyst activity loss will be 25-35 percent.

NH_3 in the cleaned flue gas is adsorbed, mainly, by the fly ash, which is precipitated in the dust collection system. The most severe case reported in the literature has been the one at the Altbach/Deizisau plant (Neckarwerke). The results obtained there indicate that a NH_3 slip value of 5 ppm guaranteed in the past has been too high when firing high quality hard coal. The flue gas has a fairly low dust content of about 6-7 g/m^3. Before the 5 ppm concentration was reached in the gas, too much NH_3 was adsorbed on the dust for use in cement and concrete applications.

The accepted upper value for NH_3 in fly ash for cement and concrete companies is, at present, set at 50-100 mg/kg. The natural content of ammonium compounds in fly ash is 5-20 mg/kg. In cases of low ash coal, the NH_3 slip must be limited to 2-2.5 ppm. Although the ammonia slip in the fly ash and formation of ammonium salts on downstream facilities are possible side-effects of the SCR processes, the ECE NO_x Task Force[10] concluded that by the controlled operation of the plant, the fly ash quality can be guaranteed and the formation of the ammonia salts can be reduced.

Austria

Two hard coal and/or natural gas-fired units of Dürnrohr Power Station started to operate high dust location SCR plants.[35] At the end of 1988, these two units had an operating experience of 2,254 and 9,846 hours respectively. The guarantee and performance tests following the first two years of operation resulted in 81.5% NO_x reduction efficiency (guarantee 80%) and an NH_3 slip of <1 ppm (guarantee 5 ppm or less). The fresh fly ash, collected by the ESP before FGD, contains less than 50 ppm of ammonia and is sold to the cement industry without problems.

The Netherlands

The Netherlands seems to have experienced mixed results with demonstrations of SCR technologies, depending on the particular system.

Conventional SCR/Gelderland Power Station.

Within the framework of an agreement between the Dutch Electricity Generating Board (SEP), the Ministry of Environment and the Provinces to limit NO_x emissions to 30,000 tons/year by the year 2000, the first national demonstration of a retrofit high dust SCR system was conducted at EPON-Nijmegen (Gelderland) Power Station No. 12.[36] In this first long-term SCR demonstration project in the Netherlands, a positive experience was obtained.

This is a pulverized coal-fired, arch-fired furnace with a total capacity of 130 MWe. The SCR plant handles 50% of the flue gases. The start-up of this demonstration project was in 1985. The content of ammonia salts on the fly ash was measured first on a daily basis and later twice per week. In the first two years, the NH_3 content in the fly ash was ~20 mg/kg of fly ash. A NH_3/NO_x molar ratio of 0.80 appears to be used. For some time the plant was operated at an outlet concentration of 100 mg NO_x/m^3 flue gas (6% O_2). Under these conditions, a NO_x removal efficiency of about 88% was achieved.

In the Netherlands fly ash is used in a number of applications, including concrete production, lightweight aggregates, and fabrication of building stones. Ammonia contamination could lead to problems when utilized.[36] In order to collect fly ash with higher ammonia levels for analysis and possible testing in its applications, a series of tests was conducted involving a temporary increase in the NH_3/NO_x molar ratio to intentionally cause higher ammonia slip (i.e., above the design value of 5 ppm maximum). Immediately after the increase of the NH_3/NO_x ratio the ammonia content in the fly ash rose to an average of 50 mg/kg, and further increase in the NH_3/NO_x ratio to 0.90-0.95 and operating SCR under these conditions resulted in the production of fly ash with an ammonia content of 160 mg/kg. When ammonia injection was reduced to the normal NH_3/NO_x ratio of 0.80, the fly ash ammonia content immediately dropped back to about 20 mg/kg. The general conclusion was that 80% NO_x reduction can be achieved in this particular demonstration SCR installation without consequences for fly ash utilization.[12]

SCR in Air-Preheater.

Hüttenhofer et al.,[37] specifically mention experience with SCR in the air preheater of an unnamed coal-fired power station in the Netherlands, where it was demonstrated that NH_3 slip was one of the major problems experienced. It is assumed that the power plant in question is Buggenum (Maas) Unit 6. In order to limit the ammonia content of the fly ash to values of ~200 mg/kg, the NO_x reduction potential had to be reduced far below the maximum attainable level of 50 percent. Perhaps this could be ascribed to the fact that the use of catalytic converters in an air preheater differ considerably from standard SCR reactors, especially regarding catalyst operating temperature and NH_3

adsorption / desorption processes.[37] However, the air preheater arrangement has the advantage that no additional casing is required to accommodate the catalytic converter. The catalytic converters in this configuration fulfill a heat transfer function in addition to the function of NO_x abatement.

Such an arrangement was tested and demonstrated in a full-scale demonstration operation by a large Dutch independent power producer EPZ, in an agreement with the Dutch Electricity Generating Board (SEP), at their Buggenum Power Station. Two Rothemühle air preheaters of Boiler No. 6 with an output of 200 MW were equipped with Siemens catalytic converters. NH_3 injection on both the flue gas side and the air side was tested.

Acceptance measurements as well as operating results and experience following one year of operations were reported. A NO_x reduction efficiency of about 50% was achieved by NH_3 injection on the flue gas side only. The NH_3 slip was 3.2 ppm with fresh catalyst, and ~90% of this was deposited on the fly ash with a resulting fly ash NH_3 content of 250-300 ppm. After about a year, NH_3 slip increased by about 7 ppm at 30% NO_x reduction rate. Simultaneously, the NH_3 content on the fly ash increased to about 600 ppm. By dosing with ammonia on the air side, it was possible to achieve initially about 30% reduction efficiency. However, the NH_3 slip was more than 10 ppm, and the NH_3 content on the fly ash had already risen to 1000 ppm. Consequently, it was not possible to take the full advantage of the theoretical potential for the improvement on the flue gas side injection.

While there are some operating space and costs advantages to an air preheater SCR in comparison with more conventional SCR systems, there seem to be many disadvantages as well. As the available catalytic converter volume in this system is significantly lower, only 30-50% NO_x reduction efficiencies are achievable-much lower than the typical 80-90% for other, separate SCR reactors. Furthermore, the resulting NH_3 slip of 5 ppm and higher significantly exceeds the NH_3 slip of <2 ppm achievable in conventional SCR plants. This results in a high NH_3 loading on the fly ash (range of 200-1,000 ppm), rendering such ash unacceptable for cement and concrete use. For these reasons, the use of an air preheater SCR arrangement is limited to gas firing or coal-fired power plants in which only low NO_x reduction efficiencies are required and in which a high NH_3 content in fly ash does not play a significant role.[37]

Results of laboratory testing and problems encountered during the use of ammonium-contaminated fly ash from this station when concrete mortar were prepared, when concrete floors were poured, or when tests were carried out at a production facility for sintered artificial aggregate,[38] are reported later in this section.

Future SCR Installations in the Netherlands.

In a paper presented at the 1993 Joint Symposium on Stationary Combustion NO_x Controls[39] that discusses primarily Dutch experience in optimization of primary NO_x control measures, some future SCR plans are mentioned. According to the authors, the building of two SCR plants has been planned, one to be built at the Gelderland-13 power station (605 MW) and scheduled to be on stream in October 1994. It was also noted that SCR systems mounted in the air preheater (high dust) have been considered for two 600 MW coal-fired boilers. It was felt that the results of a one-year demonstration program at the Maas-6 185 MW coal-fired power station left many uncertainties, and that it is almost certain that this technology will not be applied for the 600 MW units.

SNCR-U.S. Experience

According to EPRI[8], SNCR is generally considered commercial for smaller, base-loaded plants fired by natural gas or low-sulfur oil. The commercial viability for coal-fired applications is still being determined. Table 5-7 lists SNCR retrofits completed, in operation, and planned on domestic utility boilers. Only three coal-fired boilers (Arapahoe 4, Valley 4, and Salem Harbor 2) have been retrofit and all are currently demonstrations. However, a wide range of oil- and natural gas-fired units also have been retrofitted, and many SNCR performance issues, such as temperature window and reagent mixing, are independent of the fuel used.

NO_x reductions achieved to date on selected U.S. and European utility-scale SNCR installations exhibit a wide range in NO_x removal.[8] This illustrates that SNCR performance is highly dependent on site-specific factors.

Application of SNCR results in ammonia slip, and there is a trade-off between the NO_x emissions and the extent of the ammonia slip, resulting in the ammonia contamination of ash and NH_3 emissions from the stack. Ammonia is extremely odorous at concentrations as low as 20 ppm in the ash, and its contamination of the ash has affected ash sales at some locations.[8] It is known, that in Germany and Japan operators seek to keep levels below 5 ppm in the flue gas, and in some cases even below 2 ppm, to ensure the ash remains odor-free and salable.

From an environmental point of view, it is reported that ammonia slips in the order of 20 ppm have been considered acceptable in SNCR applications in the Los Angeles basin.[8]

Table 5-7
U.S. Utility-Scale SNCR Retrofits

Utility	Unit	Size (MW)	System Type	Fuel	System Status
LILCO	Port Jefferson 3	185	LE	Oil	Demonstration under way
LADWP	Haynes 4	235	LE	Oil/Gas	Decommissioned
	Scattergood 1 & 2	2 x 180	LE	Gas	Commercial operation
EPCO	Salem Harbor 2	80	LE	Coal	Cemonstration under way
NYSEG	Kintigh 1	680	LE	Coal	Planned
	Milliken 2	180	LE	Coal	Planned
PG&E	Morro Bay 3	330	HE	Gas	Demonstration completed
PSCC	Arapahoe 4	100	HE	Coal	Demonstration under way
SDG&E	Encina 2	110	LE	Oil/Gas	Demonstration completed
SCE	Alamitos 5	480	LE	Gas	Demonstration completed
	Etiwanda 3	320	LE	Gas	Demonstration completed
	Huntington Beach 2	215	HE	Gas	Demonstration completed
	Alamitos 1 & 2	2 x 175	LE	Gas	Commercial operation
	Alamitos 3 & 4	2 x 320	LE	Gas	Commercial operation
	El Segundo 1 & 2	2 x 175	LE	Gas	Commerical operation
	El Segundo 3 & 4	2 x 320	LE	GAS	Commercial operation
	Etiwanda 1 & 2	2 x 132	LE	Gas	Commercial operation
	Etiwanda 3 & 4	2 x 320	LE	Gas	Commercial operation
	Huntington Beach 1 & 2	2 x 215	LE	Oil/Gas	Commercial operation
	Mandalay 1 & 2	2 x 215	LE	Gas	Commercial operation
	Redondo 5 & 6	2 x 175	LE	Gas	Commercial operation
WE	Valley 4	70	LE	Coal	Deomonstration completed

LE = Low energy.
HE = High energy.
Source: EPRI, Reference 8.

Nalco Fuel Tech's NO_xOUT

Nalco Fuel Tech experience with ammonia slip from selected coal-fired utility boilers equipped with NO_xOUT SNCR is shown in Table 5-8.[40] NO_x reduction ranges from 40-60%, with ammonia slips ranging from <5 ppm to 40 ppm.

Table 5-8
Ammonia Slip in NOxOUT Equipped Coal-Fired Utility Boilers

Company/ Location	Unit Type	Size (Mwe)	NO_x Baseline	Reduction (%)	Ammonia Slip (ppm)
NEPCO Unit 1 Salem Harbor, MA	Front-fired	84	1.0±0.1 lb / MMBtu	~66	5-15
NEPCO Unit 2 Salem Harbor, MA	Front-fired	84	1.0±0.1 lb / MMBtu	~66	<10
NEPCO Unit 3 Salem Harbor, MA	Front-fired	156	1.0±0.1 lb / MMBtu	~66	<10
WEPCO Valley Power Plant Milwaukee, WI (D)	Wall-fired	70	725 ppm	60	<5
Niagara Mohawk Oswego, NY (D)	T-fired	85	0.75-0.90 lb / MMBtu	45-55	10-40
RWE C2, Germany	T-fired	75	150-175 ppm	40	<5
RWE, Germany	T-fired	150	200-250 ppm	50	<10

Source: Reference 40.

NEP/Salem Harbor.

The results from demonstration of Nalco Fuel Tech's NO_xOUT process at NEPCO Salem Harbor No. 2 Unit and WEPCO Valley No. 4 Unit at both high and low loads have been reported in detail.[9] For Valley Station, it was noted that: "_ while gas phase analyses for ammonia slip generally showed very low or non-detectable levels, samples of the fly ash showed levels of ammonia significantly above the no-effect industry standard of 80 mg/kg."

It was also mentioned that while this perhaps would not be a problem if the ash was landfilled, it is realized that when such ammoniated ash would be used as a pozzolanic substitute or in other reuse applications, supplemental processing would be required. The ammonia slip at high load at Salem Harbor was higher than that measured at Valley Station: however, no data for ammonia in fly ash were reported.

Further experience with the NO_xOUT process installed at the three NEPCO Salem Harbor units has also been reported.[41] While these confirmed previously reported data regarding NO_x reduction experience (50-75% range), the ammonia slip was substantially higher, depending on the load and NH_3/NO_x ratio, than that reported earlier. For Unit 1, for example, NH_3 slip ranged up to 70 ppm at full load; at intermediate load it was nominally 100 ppm; and at minimum load it varied from 25 ppm to nearly 240 ppm. At Unit 2, the unit tested and evaluated most extensively, an NH_3 slip of 12-48 ppm was measured at full load with a corresponding NH_3/NO_x ratio 1.0-2.5. At intermediate load, NH_3 slips were in the same range as those measured at full load (i.e., 22 ppm at an NH_3/NO_x ratio of 1.8). At minimum load, ammonia slip increased relative to full or intermediate load. Ammonia emissions of 54 ppm and 66 ppm were recorded at NH_3/NO_x ratios of 1.4 and 1.8, respectively. Review of the long term test data showed that NH_3 slip levels were generally <30 ppm when firing low sulfur coal. The widest variations in NH_3 slip were seen at high loads, reflecting the wide variation in NO_x emission levels also seen at these loads.

At a recent EPRI/EPA Joint Symposium[42], further, up-to-date operating experience on Units 1 and 3 was reported. On Unit 1, where SNCR was used in combination with LNB, the SNCR system provided an additional 40% NO_x reduction from the LNB baseline (50% NO_x reduction at loads above 60 MW) at a molar N/NO ratio of 1.2. Corresponding NH_3 slip levels of <10 ppm were reported. On Unit 3, LNB tests showed that NO_x reductions of nominally 10% were achieved with the burners alone. The use of OFA, at design levels, provided additional NO_x reductions ranging from 42% at full load to 4% at a minimum load relative to the LNB baseline. The SNCR system provided NO_x reductions of 33% relative to the LNB/OFA baseline of 0.55 lb/MMBtu, at a molar N/NO ratio of 1.3. Ammonia slip under these conditions was <5 ppm.

Unfortunately, no data on NH_3 deposited on fly ash as the result of NH_3 slip were reported in any of these papers. However, another report[19], based on personal communication with utility personnel, indicated that during long-term tests performed at Salem Harbor, ash ammonia concentrations measured over two weeks period varied between 335 and 1,554 ppm.

NOELL/PSCC Arapahoe

Another SNCR system, supplied by NOELL Inc., has been installed and is undergoing demonstration at PSCC's Arapahoe Unit 4, with support from both DOE and EPRI. The SNCR here is only a part of an integrated NO_x/SO_x emission control system involving, besides SNCR, also LNB, OFA, and dry sorbent injection with humidification to remove up to 70% of the NO_x and SO_2 emissions from the 100 MW coal-fired utility boiler.[43,44] This SNCR system has an option to use either urea or ammonia (through on-line conversion of urea to aqueous ammonia). PSCC found that depending on the boiler load, it is more efficient to use one reagent or the other. When the SNCR was initially tested with urea injection into an unmodified boiler in 1992, ~35% NO_x reduction was achieved at full load, with an associated ammonia slip limit of 10 ppm. Subsequent LNB and OFA retrofit alone demonstrated a NO_x reduction of nearly 70%, with further incremental reduction when used in combination with SNCR. The integrated system is still undergoing testing, and is expected to be completed by summer of 1995.

While the ammonia slip was limited to 10 ppm, no information is given about ammonia contamination of fly ash in these papers. However, another paper[19] mentions a full-scale sample obtained from the fabric filter hoppers while SNCR was operating on Arapahoe Unit 4 under a 10 ppm NH_3 slip limit. That sample had 285 ppm NH_3 in the ash.

ABB Simulation

The potential for increased ammonia bisulfate formation and contamination of fly ash, together with fouling of the downstream equipment, and increased N_2O formation as a result of urea injection, is being discussed by ABB Combustion Engineering,[45] based on simulation work conducted at the USPPL's Boiler Simulation Facility. Concern is expressed with respect to high and variable levels of ammonia slip that can be produced by commercial SNCR systems It is mentioned that samples of fly ash from the simulation test runs were examined for NH_3 and ammonium bisulfate content, but unfortunately no data are given. The report note, however, that: "High ash NH_3 content (>5 ppm) would affect the sale of ash used for cement application and also could result in off gassing of NH_3 if the ash is stored or landfilled."

PSE&GC/Mercer G.S.

A three-month demonstration of urea-based SNCR was conducted at this station, on a 321 MW, pulverized-coal (and/or natural gas) fired, wet-bottom, continuously slagging boiler, using the mobile NO_xOUT process unit.[46] Ammonia slip was restricted to 5 ppm (corrected to 7% O_2) as a control measure for avoiding pluggage of the unit's air heaters, preventing odorous emissions from the plant and minimizing potential ammonia deposition on fly ash. Under these conditions, 38% NO_x reduction was achieved with SNCR alone. Fly ash samples were taken before and after the air heaters to gain information on how much free NH_3 was bound to the ash. At full load when coal -fired, and at the gas phase concentration (slip) of NH_3 at 5 ppm, fly ash samples had NH_3 levels ranging from 25 to 75 mg/kg (ppmw) with an average of 50 mg/kg. It was concluded that the amount of NH_3 on the fly ash during the demonstration would not impact the sale of fly ash.

Atlantic Electric/B.L. England Station

Another short-term trial using NO_xOUT SNCR, this time on a cyclone-fired boiler, has been reported by Atlantic Electric in their B.L. England Station.[47] In this trial, 30% NO_x reduction at the stack was achieved with an ammonia slip as (measured at the economizer outlet) maintained most of the time at 5 ppm or less. Ammonia slip measurements at the stack were found to be negligible (<1.5 ppm). It was assumed that this was due to the gaseous ammonia adhering to fly ash particles. A single fly ash sample was analyzed during the NO_xOUT trial, and ammonia concentrations were measured at 336 ppm. (No ammonia was present in the vitrified bottom ash sample taken at the same time. Atlantic Electric reinjects their fly ash into the furnace and all ash exits the boiler as bottom ash.)

SNCR-European Experience

In Europe, as in North America, in an increasing number of power stations, secondary control measures are considered and applied to meet strict NO_x standards. SCR is a dominant post-combustion technology used on coal-fired utility boilers in Europe, with SNCR only a very distant second. In 1990, out of total 140 such operations, based on a number of units, 92% were SCR-based, 7% SNCR-based, with 1% using some other techniques. Considering the capacity of these operations, the numbers lean further in the direction of SCR with 94% of the total capacity employing and only 5% using SNCR processes.[30]

Among the European countries where there is some experience with either commercial or demonstration SNCR operations are Austria, Denmark, Germany, Holland and Sweden. In Austria, according to the IEA Coal Research database on NO_x installations in 1990,[30] a total of 600 MWe of coal-fired capacity (out of a total capacity of 2,000 MWe) was equipped with SNCR (versus 1,000 MWe with SCR). In

Denmark, there was no commercial secondary flue gas treatment system for NO_x reduction in operation in 1990, but several pilot and demonstration tests were carried out. One full-scale ammonia-based SNCR test was carried out during 1988 at Vendsyssel block 1, NEFO, and a test using urea was scheduled for another plant for 1989-1991.

Germany has the largest installed capacity of NO_x control measures. Of its 46 GWe coal-fired total capacity, 33.7 GWe is fired with hard coal. Although almost all German utility boilers are equipped with combustion operation modifications for hard coal-fired boilers (such as LNB, air staging and operational optimization), these measures have not been sufficient to achieve the stringent emission standards. Consequently, most hard coal-fired boilers in Germany (it is not said in the referenced material, but it is assumed that all this information concerns former FRG prior to unification) are equipped with both combustion modifications and SCR. At the end of 1989, there were about 100 SCR units, approximately 26 GWe, installed on hard coal-fired plants.[31] For most of the brown coal-fired operations (12.3 GWe, or about 27% of the total German capacity), it has been possible to reduce NO_x emission to the acceptable levels using just combustion modifications. Where it was not possible to reach the standards, however, SNCR processes using different chemicals and systems have been tested and implemented on 1 GWe of commercial brown coal-fired capacity. In comparison, there are only few SCR-equipped brown coal plants in Germany, representing about 0.5 GWe.[30]

In the Netherlands, SNCR tests with urea injection were carried out on EPZ's Buggenum Power Plant unit 6 (220 MWe). As of 1990, there were no commercial SNCR plants in operation in Sweden, although it was tested on FBC as well as pulverized fuel boilers. Full-scale tests of a number of NO_x reduction technologies, including SNCR, were planned for 1990-91 at the tangentially-fired boiler at Malmö Energiverks' Limhamnsverket.[30] Commercial European SNCR plants as operated in Austria and Germany are shown in Table 5-9; full-scale SNCR tests carried in Denmark, the Netherlands and Sweden are summarized in Table 5-10.[10] The NO_x reductions achieved, operating experience and problems encountered during start-up have been reported.[6] Unfortunately, no comments are made with respect to the quality and impact on utilization of fly ash from these facilities.

Table 5-9
Commercial SNCR Installations in Europe

Plant, Utility	Electric Capacity (Mwe)	Fuel	Reagent	NO_x Reduct (%)	N/R **	Start-up Year	Comments
Austria							
St. Andrä 2, ÖDK	110	lignite	aqueous ammonia	40-60	R	1989	DBB tangential firing
Zeltweg, ÖDK	137	hardcoal / lignite	aqueous ammonia	40-60	R	1989	DBB tangential firing
Riedersbach 2, OKA	160	lignite	urea	70	R	1987	
FHW Mitte, Salzburger Stadtwerke	112 *	lignite	urea	NA	R	1989	
Belgium							
Langer Brugge 19	124	NA	ammonia	80	R	1991	
Germany							
Herne IV, STEAC	500	hardcoal	ammonia	> 50	N	1989	DBB opposed wall firing
Mainz 1, Kraftwerke Mainz / Wiesbaden	100	hardcoal	ammonia	> 85	R	1989	WBB
Marl 3, VEBA	75	hardcoal	ammonia	30	R	1986	WBB with fly ash recirculatin
Offleben II C, BKB	325	lignite	urea, methanol	NA	R	1988	

* MW thermal capacity.
** New / retrofit installation.
Source: Reference 10.

Table 5-10
Full-Scale Demonstration SNCR Tests in Europe

Plant, Utility	Country	Electric Capacity (Mwe)	Fuel	Reagent	Test Period
Vendsyssed 1, NEFO	Denmark	130	hard coal	ammonia	1988
Buggenum 6, EPZ	Netherlands	220	hard coal	urea	1989
Öresundsverket, Sydkraft	Sweden	50	hard coal/ wall-fired	urea + additive (NO_xOUT)	1987
Västerås, Västerås Stads Kraftvärmeverk	Sweden	55	hard coal/ wall-fired	cyanuric acid, urea	1988

Source: Reference 10.

Generally, with an increasing number of European countries and power plants actively considering post-combustion measures to reduce NO_x, there are concerns with respect to NH_3 absorption of fly ash. The maximum acceptable concentrations are under discussion and the consequences for fly ash utilization in relation to the odor threshold value, and impact of NH_3 on the manufacturing process and quality of the products are being considered. In Denmark, 200 mg/kg is considered the maximum acceptable limit in the SNCR processes.

Investigations of Ammonia-Contaminated Fly Ash

In most of the work and papers noted earlier, fly ash contamination with ammonia and its impact on ash utilization, if discussed at all, took only a secondary importance to the concerns related to the operation and maintenance of the boiler, the SCR systems, and of the downstream equipment.

In a personal communication from Germany from VGB (Association of Power Plants Operators) it was confirmed that the main problem of SCR with respect to the fly ash properties is the amount of ammonium salts on the fly ash.[48] The amount depends on the loss of NH_3 in the catalyst. It is noted that in some cases a relatively sudden increase in NH_3 contamination of ash was observed due to a quick reduction of the activity of the catalysts when they approach the end of their life span. Therefore, a steady control of the loss of NH_3 is recommended.

The maximum acceptable amount of NH_3 in fly ash depends on the intended use. According to VGB,[38] if fly ash is used as an addition to ready-mixed concrete, an amount of up to 150 ppm NH_3 is usually no problem. However, this could be unacceptable if the fly ash is used indoors or in otherwise confined spaces, such as in underground mining mortars. It is also noted that the cement manufacturers in Germany are cautious in general as they do not know where their cement is used. In special cases, where no air exchange takes place, odor can be a problem. Nevertheless, it is reported that even with NH_3 contents higher than 150 ppm neither health problems nor negative impact on concrete properties has been observed so far. Therefore, no limiting value for NH_3 content in fly ash is set in German standards and recommendations.

There are only a few papers[49,50,51] mainly authored by VEBA Kraftwerke Ruhr engineers and scientists, that address NH_3 fly ash contamination and its impact on its utilization in any useful detail. VEBA, a major German utility, realized that a negative SCR influence on the quality of the fly ash would have serious consequences for its disposal and use. Hence, before and after commissioning of the SCR plants the fly ash quality was monitored.[51] Daily SO_3 and NH_3 measurements before and after the commissioning of an SCR plant were made. In this case, the SO_3 content of the fly ash rose from 1 to 1.5% while the NH_3 increased from 10 to 15 ppm. The slight rise in NH_3 content by ~5 mg/kg reveals that this is not due to precipitated ammonium bisulfate. Such a slight increase in the NH_3 content of the fly ash is reported to be typical for a well-adjusted SCR plant with fresh catalyst. It has to be stressed, however, that this does not have to be the case at the later stages of the SCR plant operation, especially as the catalyst becomes fouled, poisoned and plugged, and as it approaches the end of its life span.

According to VEBA, an SO_3 content up to the limit value of 4% does not endanger the quality of fly ash. The rise can be attributed to condensed sulfuric acid, and especially to small fly ash particles. This change in SO_3 content of the tested fly ash was observed over a period of 12 months. The SCR plant was not in operation for several months, so that its influence was visible. Of particular note in this period is that the free lime content of the fly ash, which is subject to the prescribed daily check (limit value 1.5%) behaves inversely to this. An increased SO_3 content in fly ash reduces the free lime content.

In another VEBA paper, it is pointed out that as fly ash is so susceptible to the NH_3 contamination, the measurement of NH_3 content of the downstream fly ash that under normal operating conditions is <50 mg/kg, and that under unstable conditions can increase significantly can be used in qualitative monitoring of the amount of NH_3 slip and thereby the behavior of the SCR plant.[6]

In a series of experiments at VEBA's Buer Power Plant in Scholven, artificial NH_3 slippage to values as high as 12-26 ppm was introduced in order to study its downstream effects. Under these conditions, only ~65% of the slippage was found as deposits on the fly ash, a figure lower than up to 80% reported earlier by other researchers. In a later paper concerning the same station, but perhaps a different unit, a capture of 80% NH_3 in the fly ash was noted.[49] Some of the NH_3 slippage was therefore deposited on the air preheater plates, or progressed downstream. After the experiments with increased NH_3 slippage, it was then observed that the NH_3 stored in the air preheater was released back to the flue gas. After the NH_3 injector was turned off, the NH_3 concentration in the fly ash was seen to decrease.

At Buer, fly ash is separated from the flue gas stream in five-stage ESP. Even at a gas phase concentration of 5 ppm upstream from the ESP, there was still no detectable NH_3 in the gas phase downstream. It is assumed that NH_3 undergoes a secondary reaction with acid fly ash components or is absorbed on the fly ash. The NH_3 bound to the solid material is removed with the fly ash from the flue gas. The fly ash is separated from the flue gas with an overall efficiency of >99 percent. According to VEBA, the NH_3 separation trails slightly behind, because NH_3 tends to deposit itself more readily on the fine grain fractions of the ash that are not separated until the rear area of the ESP. Under the conditions prevailing at Buer, the concentration of NH_3 in the precleaning, intermediate cleaning, and postcleaning stages is approximately in a ratio of 1:2:3.

From the fly ash study conducted at the Buer P.S., the quantity of dust and NH_3 from the individual stages of the ESP, and the quantities introduced into the FGD system were determined. At a pure gas dust content of 50 mg/m^3, corresponding to a dust load of 25 kg/h, this means that at a NH_3 slippage downstream from the air preheater of 5 ppm, which is an equivalent of about 2,100 g/h NH_3, only 6 g/h reaches the FGD plant with the pure gas. The increased NH_3 slippage in July 1986, corresponding to about 3 ppm, was the result of the contamination of the catalyst, causing the NH_3 content in the fly ash to increase to 50 mg/kg. This did not have any repercussions on the FGD wastewater.

The Institute for Building Research of the Aachen University[52] has conducted a literature study on international standards and other topics concerning the effects of NH_3-bearing fly ash from SCR equipped power stations upon concrete made with such fly ash as an additive. This study has been reported by VEBA.[49] At the time of the study (1987), it was found that no studies regarding the concrete-making properties of fly ash contaminated with ammonium salts had been published.

VEBA Study

Samples of fly ash with different levels of NH_3 content were taken at the Buer Power Station, incorporated into mortar and concrete, and tested, with particular attention to the concrete properties such as:

- Properties of fresh concrete (setting behavior, workability);
- Air voids content (voids formed by ammonia gas); and
- Strength (as affected by changes in the pore system).

The chemical compositions of the fly ash samples used in this study are shown in Table 5-11.

Even in the absence of added NH_3, a natural NH_3 content of 5-20 mg/kg of ash was found to be present in the Buer fly ash, as indeed it is in ash from most coal-fired power stations. The reference sample No. 1 represents such a material. Samples 2 and 3 contained 28 and 53 mg NH_3/kg of fly ash, corresponding to an NH_3 slip of 2 and 4 ppm. For the 5 ppm slip, the limiting value for which most of the German SCR installation appeared to be designed at that time, the NH_3 content in the fly ash would be 70 mg/kg. Under trial operating conditions, the ammonia dosage was briefly raised to the technically possible maximum, resulting in NH_3 contents in the ash that ranged from three- to almost five-times the limiting value (Samples 4 and 5).

Mortar Investigations

Water requirement and setting characteristics were tested on mortars consisting of mixtures of Portland cement and fly ash samples under investigations in the proportions 4:1. Table 5-12 shows no significant differences were found with respect to water demand in the various fly ash mixes. The water demand of the pastes containing fly ashes was slightly lower than that of the cement paste. As expected, the use of fly ash in all cases resulted in some retardation of the initial set.

The early stiffening behavior of cement/fly ash mortars was investigated by measuring the relative viscosity. The data give no indication of any chemically induced reactions that may have resulted in increased stiffening. It was stated that the differences in early stiffening behavior of the respective mixes were due to physical differences (fineness, specific surface area) between the fly ash samples and not the NH_3 contained in the fly ash.

Table 5-11 Chemical Composition of Coal Fly Ash Samples Used in VEBA Study

Constituents		**Sample Number**				
		1	**2**	**3**	**4**	**5**
SiO_2	%	47.2	47.8	47.1	47.3	47.7
Al_2O_3	%	27.2	27.2	27.0	27.4	27.3
Fe_2O_3	%	8.3	7.6	7.2	7.2	7.6
CaO	%	3.0	3.1	3.0	2.9	2.9
MgO	%	2.3	2.2	2.3	2.3	2.2
Na_2O	%	1.3	1.4	1.4	1.3	1.4
K_2O	%	4.3	4.1	4.3	4.1	4.2
TiO_2	%	1.1	1.0	1.2	1.0	1.1
P_2O_5	%	0.5	0.3	0.3	0.3	0.3
SO_3	%	0.6	0.6	0.6	0.5	0.6
C	%	3.4	3.9	3.5	4.1	3.1
LOI	%	3.7	4.2	3.9	4.4	3.4
SO_3	%	0.57	0.56	0.56	0.52	0.56
Cl	%	<0.01	<0.01	<0.01	<0.01	<0.01
CaO (free)	%	0.45	0.44	0.41	0.38	0.47
NH_3	mg/kg	19	28	53	180	289

Source: Reference 49.

Table 5-12
Investigation of Mortar: Setting, Water Requirement and Soundness

Sample No.	NH_3 (mg/kg)	Setting		Water Demand (%)	Soundness	
		Initial (min.)	Final (min.)		Boiling Test*	Needle Test**
1	19	150	240	28.6	satisfactory	0.5
2	28	180	240	28.8	satisfactory	1.0
3	53	180	230	28.4	satisfactory	1.0
4	180	180	240	28.6	satisfactory	1.0
5	289	170	250	28.8	satisfactory	1.0
PC 45 F		140	210	29.0	satisfactory	not deter.

* DIN 1164
** DIN EN196 T.3
Source: Reference 49.

The compressive strength of mortars at 2, 7, 28 and 90 days was determined according to DIN 1164. The reference mortar with Portland cement had a w/c ratio of 0.5. The cement-to-fly ash ratio was again 4:1; the water content was kept constant, corresponding to that of the reference mortar. The spread (consistency in the German flow table test) and bulk densities of the fresh mortar were determined as well in Table 5-13. No indication of any appreciable effect of NH_3 in the fly ash on the tested mortar characteristics was observed.

Concrete Investigations.

Concretes containing fly ash were made and tested for air voids content according to DIN 1048. The concrete test specimens were placed in the pressure vessel and compacted. The voids content was found to be in the range from 3.2-4.2% by volume. There was no indication of any additional voids due to ammonia formation. The average compressive strengths of 12 test cubes of each of the investigated concrete mixes, conditioned at 95% relative humidity and 20°C for 7 days, followed by storage at 65% relative humidity and 20°C until testing. Compressive strengths at 2,7,28 and 90 days were determined. There was no ascertain able effect due to the ammonia in the ash on the strength of the concrete.

Table 5-13
Investigation of Mortar: Spread (Consistency), Bulk Density of Fresh Mortar and Compressive Strength

Sample No.	NH_3 Content (mg/kg)	Spread (mm)	Bulk Density (kg/m^3)	Compressive Strength (N/mm^2)			
				2 Days	7 Days	28 Days	90 Days
1	19	155	2243	18.9	37.2	51.6	67.7
2	28	150	2226	21.6	42.0	51.9	64.9
3	53	145	2234	21.2	36.4	58.7	72.0
4	180	145	2218	20.7	41.3	53.9	70.9
5	289	150	2251	18.0	36.3	52.8	71.3
PC 45 F		175	2310	not det.	45.1	59.1	no det.

Source: Reference 49.

The results of the permeability (water tightness) testing of all concrete samples were below the limiting value of 50 mm specified for watertight concrete grade B II by German standards. The NH_3 content of the fly ashes employed in the respective mixes did not appear to have any effect on the results.

The investigation of the fly ash samples with various levels of the NH_3 content and the tests performed with mortar and concrete have definitely shown that fly ash with NH_3 contents ranging as high as 300 mg/kg have no adverse effect on the properties relevant to concrete technology. Ammonia gas, which is formed by reaction of the ammonium salts adhering to the surface of the fly ash particles with the calcium hydroxide formed in the cement hydration process, does not affect the setting, the soundness, the air voids content, or the strength of mortar and concrete to any quantifiable extent.[49] The study reached the more general conclusion that fly ash from coal-fired furnaces operating with accredited SCR installations does not affect the properties of concrete in which it is used as an additive.

Ammonia Odor.

Even if NH_3-contaminated fly ashes from SCR plants do not affect concrete properties and applications, ammonia odors potentially emanating from such concretes and its possible harmful effect on human health is a concern.

The odor threshold for ammonia is 1-5 ppm, and the current recommended 8-hour occupational standard is 25 ppm.[31] A number of investigators have studied the human health effects of acute NH_3 exposure of varying durations and concentrations. Although in no case is an ammonia concentrations less than 30 ppm found to have adverse health effects on humans, it does not mean that such an exposure would be tolerated in the working environment. Another VEBA paper seems to be the only one that directly addresses the problem of ammonia odor in concrete, and describes an experimental program undertaken to explore this in more detail.

The most extreme, yet fairly typical case was selected, that of concrete screed (flooring) placed in a closed room. Such material is usually prepared with a high fines level, and therefore with a high fly ash content. It is usually pumped through pressure lines into more or less confined space, and the gaseous ammonia cannot be easily dispersed or its concentration diluted as a result of air change. In the experiments,[50] a screed mix consisting of 287 kg Portland cement, 123 kg fly ash, 1,612 kg river sand and 1,70 l water per 1 m^3 was prepared in a customary 2 m^3/h screed mixer, pumped through a hose into a window-less room of 64 m^3 where it was distributed over a floor area of about 22 m^2, and leveled with a power float. Two probes suspended 0.3 and 1.5 m above the floor were provided to sample the room air. The amount of NH_3 salt contamination in the fly ash naturally influenced the amount of ammonia gas in the room air. The NH_3 salt contamination was introduced into the screed in three different ways:

- Test series A-Through use of fly ash samples produced at VEBA's Buer Power Station by excessive addition of NH_3 up-stream of the SCR reactor, and consequently artificially high ammonia slip. Four different contaminated fly ash samples were produced at 47, 104, 249, and 314 mg NH_3/kg of ash.
- Test series B-For comparison, two uncontaminated fly ash samples were dosed with ammonium bisulfate at 106 and 256 mg NH_3/kg of ash levels.
- Test series C-Again for comparison, ammonium chloride was introduced into the screed mix, not through the ash, but through the mixing water at the equivalent level of contamination of 50, 100, 200 and 300 mg NH_3/kg of ash.

Four criteria were used in the assessment of the odor, according to German industrial guidelines:

- Subjective perception by workers, with classification ranging from 0 = odorless to 4 = unbearably odorous;
- Odor perception value threshold value 3.8 mg NH_3/Nm^3 (5 ppm) (GSW);
- Value for irritation of eyes and respiratory passages 15 mg NH_3/Nm^3 (20 ppm) (RAA); and
- Maximum permissible limit value 31 mg NH_3/Nm^3 (41 ppm) (MAK).

For experimental series A and B, the released ammonia odor was, at worst, at the very low perception threshold levels. It was claimed that the subjective assessment by the screed applicators/workers confirmed these findings. It was also found that within a day any ammonia odor completely dissipated, and was no longer detectable. On the other hand, in the series C, where NH_4Cl was introduced with the mixing water, at the 200 mg/kg addition the NH_3 concentration in the room exceeded the permissible limit level, and the NH_3 odor in the room air persisted for days, dissipating only very slowly.

It was concluded, that the use of SCR fly ash contaminated with NH_3 at levels of up to 200 mg/kg poses only a very minor encumbrance (of the order of the odor perception threshold) even in an enclosed room, and that where screening is carried out in a well-ventilated room, the odor is barely detectable. (It was noted by the authors that the artificially high 200 mg/kg level of contamination of the ash representing much higher ammonia slip than the usual guaranteed maximum of 5 ppm should not occur in the properly functioning SCR plant.)

KEMA Study

Apart from the VEBA study discussed above, the only other work addressing directly the effects of ammonia contamination of fly ash on its use in a number of established applications is a Dutch study by KEMA, the results of which were presented at EPRI/EPA 1995 Joint Symposium on Stationary Combustion NO_x Control.[38]

Three typical fly ash applications were evaluated:

- Production of concrete mortars;
- Pouring of concrete floors; and
- Production of Lytag sintered mineral aggregate.

The first two were conducted in the laboratory, the latter in an actual production facility. The potential impact of ammonia out gassing in temporary storage at the disposal site was another concern addressed. In all fly ash applications, the main areas of interest were the effects of NH_3 contamination on:

- Working conditions;
- Operational problems; and
- Product quality.

The fly ash used for this work came from the Buggenum (Maas) 6 station (with SCR in air heater) discussed earlier. Fly ashes in 100-300 mg NH_3/kg contamination range were used for most of the work.

Temporary Storage.

Fly ash samples, moistened to control dust formation, are handled at the Maas Power Station. A distinct ammonia smell during transportation of the fly ash on the conveyor belt and at the disposal point was observed. The NH_3 content of this fly ash was determined to be between 120-180 mg/kg. The measured ammonia concentration in the ambient air was in 20 ppm range.

Preparation of Concrete Mortar.

Concrete mortar with NH_3 contaminated fly ash as partial replacement for cement was prepared in a laboratory in a closed concrete mixer (Table 5-14). The ammonia concentration in the air inside of a closed concrete mixer as well as the percentage of ammonia released from the mortar as a function of mixing time was measured. Within a minute after the start of the experiment the NH_3 concentration in the air in the mixer reached 170 mg/m^3. At the end of the experiment, after 27 minutes, 10% of the ammonia originally present had been released from the mortar. Following the pouring of the cubes, the ammonia concentration in the air inside a closed vessel (where the cubes were placed) declined steadily over time.

Table 5-14
Composition of Concrete Mortar

	kg/m3
Portland Cement A	230
Fly Ash	80
Sand/Gravel	1770
Water	196
Ammonia Content of Fly Ash	300 mg/kg

Source: Reference 38.

The compressive strength and residual ammonia content of concrete cubes cast from this mix were measured following 7, 28, and 91 days of curing (Table 5-15). After 28 days, the compressive strength of the NH_3-containing cubes was 80% of the reference value, which is in the normal range. After seven days, the ammonia content of the concrete cubes was 1-2 mg/kg or 10-20% of the original amount. After 91 days, the ammonia content was at the same level as in the reference cubes.

Table 5-15
Compressive Strength and Ammonia Content of Concrete Cubes Cast with Ammonia-Contaminated Fly Ash

	Curing Time	**Compressive Strength**		**Ammonia Content**	
	(days)	**(N/mm^2)**	**(% of ref.)**	**(mg/kg)**	**(% of orig. amt.)**
Ammonia Contaminated	7	18.6	74.8	1.78	13.9
	7	18.3	73.6	0.92	8.9
	28	23.8	82.9	1.10	10.7
	28	29.6	85.2	1.40	13.6
	91	40.3	85.4	0.17	1.7
	91	40.8	86.4	0.20	1.9
Reference	7	24.8	—	0.37	—
	28	34.7	—	0.30	—
	91	47.2	—	0.37	—

Source: Reference 38.

Pouring of Concrete Floors

Three concrete floors were made and poured (in a laboratory) with concrete (Table 5-14), including fly ash with three different levels of contamination. One floor was poured in open room with natural air circulation. Fly ash with 300 mg/kg NH_3 was used, and during the pour an ammonia concentration of 5-10 mg/m^3 was measured close to the surface of the floor. At this level, hardly any ammonia smell was noticeable in the room. The other two floors were poured in a confined room with fly ash at 100 and 200 mg/kg NH_3 contamination. During the pour, the ammonia odor in the air in the confined rooms was clearly noticeable. Within a short period of time after the pour, however, the ammonia smell dissipated. This observation confirms the findings of the VEBA study.

Manufacture of Artificial Sintered Aggregate.

The impact of the NH_3 contamination (at 300 mg/kg) on production of Lytag sintered artificial aggregate was assessed in a 32 tons/hour plant. Ammonia levels at different steps of the manufacturing process were measured in two separate experiments in both in the product and in the air are shown in Table 5-16.

Near the transfer point between the two conveyor belts, bursts of ammonia smell were observed, with levels as high as 38 mg/m^3. It was found that green pellets on the pelletizer and the conveyor belts sometimes smelled and sometimes did not smell, although all contained about the same levels of ammonia. The ammonia concentration in the homogenizing air from the silo was negligible. The off-gas from the sinter plant, however, contained a very high ammonia concentration (50 to 75 mg/m^3). Most of the ammonia was captured in the fabric filter, but the emission with the off-gas was not negligible (5-13 mg/m^3). The dust in the baghouse had an extremely high ammonia content, values as high as 11.6 g/kg and 13.7 g/kg being found.

Table 5-16
Ammonia Measurements During Lytag Production from NH3-Contaminated Fly Ash

Condition	Experiment 1	Experiment 2
Homogenized fly ash	304 mg/kg	—
Homogenizing air	< 0.5 mg/m^3	—
Green pellets pelletizer	324 mg/kg	295 mg/kg
Green pellets transfer point	315 mg/kg	300 mg/kg
Ventilation air / pelletizer	—	0.1 - 1.0 mg/m^3
Air near transfer point conveyor belts	—	4 - 38 mg/m^3
Off gas sinter plant baghouse	50 mg/m^3	75 mg/m^3
Emitted off-gas	5 mg/m^3	7 - 13 mg/m^3
Dust collected in baghouse	13,700 mg/kg	11,600 mg/kg
Lytag pellets	< 0.5 mg/kg	—

Source: Reference 38.

The following are some of the conclusions KEMA has drawn on the basis of their study, largely confirming and adding to the results obtained by VEBA:

- "_ hardly any odor is to be expected during disposal of fly ash containing 100 mg/kg of NH_3. Some odor nuisance may be expected at 200 mg/kg NH_3;"
- "_ surpassing the MAC value of 18 mg/m^3 is possible at 300 mg/kg NH_3 (casting mortar in confined space, sintered aggregate production);"

- "_ no impact of NH_3 contamination of fly ash (at up to 300 mg/kg levels) on product quality has been found;"
- "_ operational problems can be expected during sintered aggregate production due to the high concentration of NH_3 in the off-gas downstream of the sinter plant."

Summary

The only extensive, large scale experience with the application of SCR technology to control NO_x emissions in coal-fired power stations exists, at this time, in Germany. Although it is claimed that most of these stations continue to provide ammonia-contaminated fly ash from such operations to many established ash utilization applications (e.g., cement and concrete production or artificial aggregate manufacturing), very few in-depth studies confirm the harmlessness of such contamination and the lack of impact on the ash use exist in public domain. Based on the results of two German and Dutch studies that specifically addressed the use of NH_3-contaminated fly ashes from SCR equipped power plants, the following conclusions can be drawn:

- Mortar and concrete properties, such as setting, soundness, air voids content or strength, made with fly ash containing up to 300 mg NH_3/kg are not affected to any significant degree;
- Use in floor screeds at up to 200 mgNH_3/kg results in a very small odor nuisance (the NH_3 odor dissipates within 0.5 - 1 hour of concrete placement);
- Hardly any odor is to be expected during disposal of fly ash containing 100 mg/kg of NH_3. Some odor nuisance may be expected at 200 mg/kg NH_3;
- The odor perception value threshold value (2 - 5 mg NH_3/m^3) is probably reached at low levels (100 - 200 mg/kg NH_3) of contamination, especially in confined areas. Irritation of the eyes and respiratory passages values of (15 - 18 mg NH_3/m^3) is possible at 300 mg/kg NH_3 and could be a problem for casting mortar in a confined space, or in sintered aggregate production;
- There is no impact of NH_3 contamination of fly ash (at up to 300 mg/kg levels) on product quality; and
- Operational problems can be expected during the production of sintered aggregates due to the high concentration of NH_3 in the off-gas downstream of the sinter plant.

Despite the findings of these two studies, most of the utilities and users are still cautious in the use of NH_3-contaminated fly ashes from SCR (and SNCR) denitrification processes, and if such materials are used, a cutoff limit of 50 mg NH_3/kg of fly ash is usually employed.

There are no European standards in place with respect to the maximum acceptable concentrations of ammonia in fly ash at this time. However, such standards are under discussions, with probable maximum permissible levels of the NH_3 contamination being in the 50 - 100 mg/kg range.

In the U.S., there is virtually no experience with the use of NH_3-contaminated fly ash from SCR and SNCR NO_x control plants in concrete and cement applications, or in any other uses. Because of differences in the characteristics of North American coals versus those used by most European utilities, the effects of ammonia contamination impact on fly ash use is unknown.

At the same time, it is important to note that the negative perception associated with ammonia in fly ash in the U.S. comes from a different and quite unrelated cause: i.e., that of ESP conditioning. When such a technique is used to improve dust collection, the level of contamination can be over 1,000 mg NH_3/kg of fly ash. Typical European experience with SCR shows that contamination is an order of magnitude lower, or less than 100 mg NH_3/kg of fly ash.

6

FLY ASH BENEFICIATION TECHNOLOGIES

As is evident from the discussions in Sections 4 and 5, some of the means employed to reduce NO_x emissions from coal-fired utility boilers may downgrade its value as a usable by-product in certain markets. Factors that may impact ash quality in this way include:

- The presence in the ash of excessive unburned carbon (UBC);
- A relative reduction in the pozzolanic reactivity of ash induced by its thermal history or an increased proportion of coarse particles; and
- Contamination by ammonia or ammonium compounds formed during the application of SCR or SNCR NO_x reduction processes.

Uses of ash is an important component of ash management at many utilities. It represents both revenue enhancement and reduced disposal costs. Some utilities are currently reporting lost ash sales due to off-specification ash (high LOI) or detectable ammonia contamination. Consequently, consideration to the prevention or mitigation of the impact of ash contamination on important and sensitive utilization markets, a particular example being cement and concrete applications, needs to be given. Four approaches to minimizing the impact of reduced ash quality on ash utilization are indicated, as follows:

- Prevention of carbon accumulation in fly ash for use in sensitive markets;
- Carbon removal;
- Concentration of reactive ash fractions by removal of coarse fractions; and
- Ammonia removal.

To prevent carbon accumulation, the most effective route would appear to be optimization of the combustion processes to maximize fuel burnout. A particular benefit of this approach is that while it leads to reduction in carbon contamination it also improves combustion efficiency. A secondary approach might involve selective collection of ash.

Given that currently available NO_x reduction technologies may lead to the presence of additional carbon and other chemical contaminants in the coal ash, one possible remedial solution will be to attempt to upgrade or "beneficiate" the ash by removing or reducing the contaminants. This is an approach which is used extensively in the mineral processing industry and has also been used successfully to upgrade "problem" fly ashes for sale: for example, coarse and / or high carbon ash produced at a plant which is not base loaded.

There are several beneficiation technologies, some of which are currently under development, which potentially could be used to remove carbon from low-NO_x ash. One such technology involves electrostatic separation (similar to that used in the dust collection system of the power plant); another uses a fluidized bed technology to burn out the carbon; other approaches beneficiate the ash by air classification or flotation. These all require evaluation from both a technical and economic feasibility perspective.

In addition to the potential for producing "specification" ash from low-NO_x sources, carefully selected beneficiation opens up opportunities for the generation of new and value-added products, such as:

- Fillers (e.g., for plastics and other composites);
- Enhanced pozzolans;
- Carbon products; and
- Metals recovery.

Carbon Management in Low-NO_x Fly Ashes

For many low value-added markets for ash, unburned carbon does not present a major concern. However, in the important cement and concrete market, user demand is for low-carbon ash. This market, which comprises applications in ready-mixed concrete, concrete products, and blended cements, consumes some 65% of the fly ash currently being used in the U.S. (about 15% of all ash generated).

Use of fly ash in these applications is anticipated to grow as cement manufacturers move to increase blended cement production as a means of meeting demands for reduced carbon dioxide emissions. Further, it is a market in which fly ash faces strong competition from ground granulated blast-furnace slag.

User specifications in the cement and concrete market require fly ash to have:

- Low carbon content (LOI) to reduce chemical admixture demand and product color;
- Low variability
- Maximum pozzolanic activity; and
- Minimum property variability.

The principal national specification, ASTM C 618, which currently permits up to 6% LOI, is under review and some ash purchasers are setting much lower limits in the form of performance standards of less than 3 to 4 percent. Overall, the pressures in this competitive marketplace suggest that any reduction in quality due to low-NO_x combustion methods will exclude the ash from cement and concrete applications.

To meet these demands, it will be necessary to reduce the carbon content of ash being offered for cement and concrete applications by either: (1) optimizing combustion or ash collection conditions; or (2) removing UBC from the ash by employing some form of post-collection materials processing. Approaches to managing UBC in ash are discussed in the following paragraphs and are summarized in Table 6-1.

Combustion Optimization

Because retrofit combustion controls are the simplest and most cost-effective options available to utilities for NO_x reductions, they are the most frequently applied. In particular, the use of LNBs is the approach most employed to date in North America. To attain optimal NO_x reductions with LNBs demands that combustion equipment and all key associated systems are in good condition. Additionally, boiler design and coal properties should be suitable to staged combustion conditions. Even when all these issues are addressed in the integration of retrofit combustion NO_x controls, adverse operational impacts can occur. Among the factors that may be impacted is boiler efficiency. While this clearly affects operating costs and productivity, it is also the source of the principal impact on ash quality-namely unburned carbon (UBC).

As was discussed in Section 4, there is an inherent relationship between NO_x emissions and UBC with many low-NO_x combustion systems. This "trade-off," whereby decreases in NO_x emissions may be accompanied by an increase in UBC is a function of coal properties, excess O_2 level, coal fineness, thermal profile of the boiler, and the general condition of the combustion system. In general the following parameters apply:

- Coal reactivity-expressed in terms of volatile matter or the ratio FC/VM is the most important factor affecting the relationship between NO_x emissions and UBC. Coals with high reactivity (e.g., many Western U.S. coals) generally show no significant impact on UBC; Eastern bituminous coals may increase UBC by 3-5% or higher.
- Excess O_2-at higher levels while ensuring good coal burnout (low UBC) increases NO_x emissions; this can usually be addressed by optimized primary air balancing.
- Coal fineness-improves burnout wherever possible; reducing the size of coal particles to increase the proportion passing 50 mesh can reduce UBC. Improved maintenance of pulverizers will sustain such reductions in most cases.

Table 6-1
Comparison of Methods to Beneficiate Fly Ash by Carbon Reduction

Method	Effects on Ash Properties	Process Implications	Commercialization Status
Combustion Optimization	Target is to have no impact or an improvement in quality.	Requires combined burner, combustion conditions, coal grinding and process optimization. Can be built in to compliance optimization procedures designed for monitoring and controlling air emissions or boiler efficiency. Improved fuel efficiency real-time control of ash quality.	Boiler manufacturers are offering these systems.
Carbon Burn-Out	Low-carbon fly ash reduced variability. Pozzolanic activity? (no data).	Requires add-on combustion system. Has recovery potential. No solid or liquid wastes produced.	Pilot-scale equipment developed by Progress Materials Co., Florida. Commercial scale FBC systems available. Demonstration successful, specification ash produced in trials.
Particle Size Control			
Selective Ash Collection at ESP Discharge	Reduced coarse particle content. Reduced carbon content in some cases. Reduced variability. Minor increase in pozzolanic activity.	Requires add-on ash handling plant. Difficult to co-ordinate with ESP operating parameters. No carbon recovery possible. The first stage of the ESP accumulates most of the coarse carbon and also handles most of the ash load .	No commercial efforts that we are aware of to date. Would need selective marketing in addition to selective ash collection.
Screening	Reduced coarse particle content. Reduced carbon content. Reduced variability. Minor increase in pozzolanic activity.	Requires add-on screening plant. Low through-put and capacity with fine particulates. Carbon recovery possible. Coarse solid wastes produced.	Commercial equipment available. Previous efforts have tended to fail at commercial scale on plant through-put and

Table 6-1
Comparison of Methods to Beneficiate Fly Ash by Carbon Reduction

	Improved concrete workability.		down-time.
Grinding or Intergrinding (with cement clinker)	Reduced coarse particle content. Minor increase in pozzolanic activity. Reduced concrete workability.	Requires add-on plant No removal of carbon.	Commercial equipment available. No value added to ash for concrete because no carbon is removed
Air Classification	Reduced coarse and mid-size particle content. Reduced carbon content. Reduced variability. Increase in pozzolanic activity. Improved concrete workability. Optional value added product(s).	Requires add-on classification plant. Carbon recovery possible. Only coarse carbon removed. Solid by-product streams produced some of which may require disposal.	Commercial equipment available. Previous efforts have tended to fail at commercial scale on economics of demand for classified ash.
Electrostatic Separation	Reduced carbon content ash (<4% LOI for concrete applications). Reduced variability.	Requires add-on plant. Small volume through-put streams. Coarse carbon value added product (> 40% LOI for fuel or low-grade activated carbon substitute in waste water treatment).	Pilot scale equipment available. Separation Technologies, Inc., Massachusetts. New England Electric (Salem Harbor). Early commercialization efforts (Inculet process) did not reach market acceptance.
Carbon Flotation	Reduced carbon content ash including removal of fine carbon. Reduced variability. Uncertain impact on pozzolanic activity. Probable interference with chemical admixtures in concrete.	Requires add-on plant. Wet process. Liquid waste steams to be treated and disposed. Carbon available as a value added product .	Full scale equipment available from the minerals industry. Has been used as a component in processes that can be integrated with resource recovery. Wet processing a major disadvantage with a low-value product such as ash.

- The general condition of combustion systems-when permitted to deteriorate can increase UBC. Worn or damaged pulverizers, classifiers and coal distributors limit the options available to operators to optimize boiler conditions for minimum NO_x and UBC.

Operational optimization of boiler functions are the simplest and cheapest way of reducing UBC and hence maximizing its impact on ash utility. They also contribute to the cost savings or productivity improvements that derive from an overall program of plant O & M optimization. Operators have numerous points of control that impact boiler function and performance. Clearly, in some cases an expert operator can maintain near-optimal conditions. However, the application of advanced models or intelligent systems for boiler control improves the potential for optimization by providing real-time support to the operator. A number of such systems exist or are under development based on advanced adaptive technology.

Selective Ash Collection

Electrostatic precipitators typically have three, four, or even five fields that remove consistently finer ash fractions. Some fractions may be carbon rich. If ash from these fields can be selectively discharged, contamination of otherwise acceptable ash can be reduced.

Where carbon segregation occurs, it is not unusual to find higher levels of UBC, together with coarser particles in the first field of the ESP. However, it has been observed that some plants produce a fine lacy carbon that is found throughout the ESP, including even the last ESP field.[1,2,3,4,5] An added advantage of selective collection of ash is that the pozzolanic properties of ash improve across the ESP fields.[2,3,4,5] Therefore, selective collection could in principle produce an ash with: reduced coarse particle content, reduced carbon content in some cases, reduced variability, and increased pozzolanic activity.

Although appealing in principle, this approach can be expected to meet with a number of practical problems, in particular:

- It requires an add-on ash handling plant;
- There will be difficulties in coordinating ash collection with ESP operating parameters;
- No carbon recovery is possible;
- The first stage of the ESP accumulates most of the coarse carbon and also handles most of the ash load;
- To be effective, the approach would require selective marketing / disposal in addition to selective ash collection.

There is no indication in the public literature that any commercial efforts have been made in this direction.

Selective Marketing Based on Carbon Content

Some boilers show variable levels of unburned carbon, with "normal" production of acceptable ash being infrequently interrupted by production of excessive UBC. If ash produced under these "upset" conditions could be diverted from the materials shipped to the critical cement and concrete market, loss of that market could be avoided. To facilitate such diversion of off- specification ash, the use of "on-line" measurement of unburned carbon content in fly ash would be an advantage. Such on-line monitoring has become increasingly more important, especially following adoption of various low NO_x control technologies by utilities and resulting increases in UBC.

Various instruments have been and are being developed to monitor ash LOI.[6,7,8] One of these, the so-called "Hot Foil_ LOI Instrument," manufactured by Fossil Energy Research Corporation under license to EPRI, is still an off-line instrument, although being a small, portable bench-top analyzer, it allows flexibility in LOI determination away from laboratory facilities. The instrument yields LOI values for fly ash samples within 15 minutes by heating with electric current a small (<100 mg) sample in a foil "boat." Good agreement with the conventional ASTM LOI technique is claimed.[6]

Understandably, the trend is towards true on-line, in-duct determination of LOI. One such system providing automatic, reliable, low maintenance, on-line analysis of carbon carry-over has been reported by DiGioia and Kelly.[7] It consists of a carbon-in-ash (CAM) system with an associated adaptive duct sampling (ADS) system supplied by the CAMRAC Company. It is based on a cooperative effort funded by a number of major utilities, EPRI, and GAI Consultants, Inc., the principal contractor for the development work. The CAM is a microwave-based technology, a prototype of which has been operating at the PECO Energy Eddystone Station since April 1993. This system is being utilized in an EPRI-sponsored program to optimize boiler performance. It is a non-contact measurement technique operating at ambient temperature. Without combusting the ash carbon; it utilizes pneumatic principles and equipment for fly ash sampling, handling and transport. Microwave energy at 2.45 GHz, to which carbon-free ash has little susceptibility, but carbon is very susceptible, is used to measure UBC.

The PECO adaptive sampling system presently utilizes a single-point sampler and automatically maintains isokinetic sampling conditions over the range of unit operating conditions and duct flow variations. A multi-point system is another option, although the utility industry appears to be presently divided on whether a "trending" single-point sampler or a "representative" multi- point sampling system will meet their expectations. The measurement accuracy (percent carbon) for the CAM system compared with laboratory determination for multiple fly ashes with UBC carbon in the 1 to 11% range.

The Southern Company was one of the utilities that participated in the development of the CAMRAC equipment which automatically retrieves and analyzes fly ash samples from ducts with a cycle of time of 5 to 10 minutes. The first Southern Company CAMRAC unit is now beginning operation at Plant Hammond, Georgia.[4] This initial installation will involve comparison of LOI values for duct and ESP hopper samples, as well as comparison of analyzer results with competitive on-line instrumentation (e.g., the SEKAM analyzer from the U.K.) and with standard laboratory determinations. The cost of the CAMRAC analyzer is about $50,000; the SEKAM analyzer is about $75,000.

A potential alternative on-line measuring system is the Concarb 2000.[9] This instrument operates spectrophotometrically in a continuous manner taking multi-thousand readings per minute of both carbon and relative solids densities in the flue gas. Unlike a single-point source, the Concarb 2000 monitors a conical volume of approximately 5-feet long and 3-feet wide at the maximum. While the instrument does not appear to be commercial as yet, it is claimed that tests completed in 1994 at the Homer City Power Generating Station Unit 2 demonstrated high reliability, low maintenance costs, and easy and rapid installation. The projected unit costs are about $120,000.

Ash Beneficiation

If ash contamination with UBC cannot be prevented, economical removal of carbon may be an option to meet ash specification demands. There are a number of options available for reducing or removing the UBC content of ash by employing some form of post-collection processing, the major ones being:

- Carbon burn-out;
- Particle size control (screening, grinding, air classification);
- Electrostatic separation; and
- Wet separation (flotation).

The following paragraphs provide a description of these alternative approaches.

Carbon Burn-Out.

The simplest approach to carbon removal is to burn the ash. This has the slight advantage that some thermal value is recovered that can be used to offset processing costs. The disadvantage is the probability that the ash glass reactivity may be adversely affected.[10] This aspect of ash carbon burnout does not seem to have been considered by advocates of the process.

The principal publicly available information on the use of carbon burnout to improve ash quality for concrete applications has been reported by Cochrane and Boyd from an

EPRI-tailored collaboration project being pursued by Florida Power Corp., its subsidiary, Progress Materials Inc. of St. Petersburg, Florida, and participants Duke Power Company and EPRI.[11] Carbon content reduction by burnout was demonstrated during 1992-93 in both small scale batch processes and a 1 ton per hour prototype fluidized bed pilot plant. Ash from a range of sources containing a wide range of carbon contents was examined using these approaches with the target of attaining residual carbon content in the processed ash of <3.0 percent. The authors concluded that results obtained in pilot plant operations demonstrate the validity of the technology.

Duke Power has designed a 175,000 tons per year continuous process carbon burnout plant. Cost estimates showed that processed low-carbon ash could be competitive with "naturally-occurring" low carbon ash if the transportation differential is more than 75 miles. The advantage of this technology is that all of the ash is transformed into a salable low carbon content material meeting the LOI specifications required for the concrete market.

Physical Removal of Carbon.

An alternative approach to reduce carbon content is to employ some form of physical separation or beneficiation of ash. This has the added advantage of also reducing the proportion of coarse particles and hence offers the potential of contributing to an increase in the pozzolanic reactivity of the ash.

The ability to remove carbon by beneficiation depends upon two factors: the degree to which the carbon-rich particles are discrete, and the size and shape of the carbon particles.[1,2,3,4] UBC in some fly ashes is present in at least two general forms.[1,12,13] These two forms may be described as: (1) incompletely burned coal (coke) particles with a wide range of sizes (often >200 m.); and (2) a fine "lacy" carbon (<5 m.).

Size-fractionation (using dry or wet methods) and electrostatic separation techniques have been used to remove the coarse carbon particles. More complex processes such as froth flotation are necessary to remove or concentrate the fine carbon materials.

Processing ash to change the bulk composition or particle size distribution has long been practiced to increase reactivity, improve recovery of metal values, and in some cases to reduce carbon content (or recover a carbon-rich fraction).[1] Such processing, frequently termed beneficiation, is normally achieved through one or more common separation techniques, such as:

- Screening with or without grinding;
- Mechanical size-classification;
- Density separation;

- Magnetic separation;
- Electrostatic separation; and
- Flotation or related wet processing.

Screening.

In mineral processing, it is common practice to use screens to remove coarse particles from powdered products. In general, dry screening of powders is not economically practical at screen sizes much below 325 mesh (45 µ). This produces an immediate problem with fly ash because a large proportion of the particles (typically >50%) are finer than 45 µ. Using 100 mesh screens is effective for the removal of most of the coarse particles, many of which comprise UBC. As such, screening may be effective as part of a general ash processing scheme to:

- Reduce coarse particle content;
- Reduce carbon content;
- Reduce variability; and
- Improve concrete workability.

Grinding.

Grinding reduces particle size. While this has been clearly shown to improve pozzolanic activity,[14] it cannot be expected to contribute to removal of UBC. Indeed, it will probably result in an increase in the exposed surface area of the carbon exacerbating the problem that carbon has with interference with concrete additive properties.

Inter-grinding low carbon ash with Portland cement clinker, as an alternative to simple blending, is a common practice in the production of blended cements in many European countries.[15] This is not an option, however, with high carbon ash.

Air Classification.

Mechanical (air) classification is a more efficient method of removing coarse particles. This technique can produce a material with a maximum particle size in the range 45-30 microns. Air classification may be performed on ash for a number of reasons, such as the removal of coarse particles or the selective concentration of fine particles. In some instances, the products differ not only in particle fineness but also in carbon content. Table 6-2 presents data from air classification experiments conducted by the present authors on three different fly ashes.[2,3,4,5] As can be seen, in all cases, when coarse particles are removed, the corresponding fine fractions contain less carbon, the exact degree of carbon removal (beneficiation) being dependent on the ash source or its properties.

Table 6-2
Fly Ash Fractions Produced by Air Classification

Ash Fraction	Mean Particle Size (µ)	Elemental Carbon (mass %)	Change in Carbon Content
Fly Ash 1 - High-Fe, Bituminous Coal Ash			
Raw Ash	10.1	1.9	
>45 m.	31.0	1.9	0
<45 m.	7.7	1.5	-21%
<1 0 m.	4.1	1.3	-31.6%
Fly Ash 2 - Sub-Bituminous Coal Ash			
Raw Ash	29.8	0.56	
Classifier Rejects	47.7	0.58	+3.4%
<100 µm	17.4	0.12	-78.6%
<30 µm	8.0	0.10	-82.1%
Fly Ash 3 - Bituminous Coal Ash			
Raw Ash	23.4	2.16	
Classifier rejects	52.1	2.56	+18.5%
<45 m.	10.7	1.84	-14.8%

Sources: References 1, 2, 3, 4, 5, 16, 17.

Coarse unburned coal particles were removed by air classification in each case. Much of the residual carbon in the fine fractions (notably with the bituminous coals) was of the fine "lacy" form.[2,3,4,5] Although not established yet experimentally, it is reasonable to assume that when the carbon content of fly ash is adversely influenced by the operation of a low-NO_x system, much of the additional carbon will be in the form of coarse unburned coal particles. These particles are the most amenable to removal by size classification methods. Under these circumstances, particle size separation by air classification would be a feasible approach to reducing the carbon content of ash.

Air classification may be conducted in a number of different ways, but in general the processes rely on similar physical principles-namely, the balance of aerodynamic and centrifugal (inertial) forces on particles in a moving fluid (air). In a simple approximation, two major forces act upon particles in an air classifier:

- An aerodynamic drag-force, proportional to a projected area of the particle; and
- An inertial force, dependent upon the mass of the particle.

For particles of equal density, classification of particles into different size groups results from controlling the drag and inertial forces. Similarly, in principle, for particles of largely equal sizes, separation into density-fractions can be accomplished.

Unfortunately, fly ashes present a fundamental problem in this regard: they comprise particles of widely different densities as well as different sizes and shapes.[10] Thus, for any given set of conditions for drag and inertial force, particles of a range of sizes (with differing densities) and densities (with a wide range of sizes) will be separated into groups. When air classification is conducted for the purpose of size separation, this problem is of less concern than when density separation is desired. In principle, the presence of a wide range of particle densities among fly ash particles over a range of particle sizes, presents some constraint on the use of air classifica tion for size-separation. However, in practice, it seems that the major factor in size-separation of fly ash is the differences in aerodynamic behavior between particles of different size and shape.

This factor may benefit the desired removal of carbon particles, the larger ones of which tend to be of irregular form.

Overall, the efficiency of an air classifier is governed by its ability to fully disperse particles in a moving air stream. Only particles that are well dispersed can be separated effectively; agglomerates are rejected as oversize particles. The literature contains a number of reports of the application of air classifiers to both pilot-scale and commercial or full-scale beneficiation of fly ash. Styron[18] has reported the use of a centrifugal type of classifier to process 160,000 tons of fly ash during the period Oct. 1964 and 1970 with a product consistently of 92% passing 45 m. (325 mesh) at 84% recovery. No data on carbon content were available from this source. Use of a classifier capable of producing a fine particulate product with >95% passing 20 m. has been reported by Anderson and Jackson[19] to provide quality controlled ash for incorporation in clay brick. Cornelissen and Gast[20] report the building of a pilot plant for air classification of low NO_x fly ashes with a capacity of 2,000 kg/hr which enables the separation of ash into four fractions: coarse, medium, fine and ultra fine. Although particle size separation was effectively achieved, the system was not found suitable for carbon removal from the fly ashes examined. The authors state that:

> "Because of the different density and aerodynamic behavior of carbon compared with fly ash, coarse carbon particles appeared also in the fine and ultra fine fractions. This resulted in an even distribution of carbon over the three fractions."

This experience is not universal and may indicate that either the fly ash or the classifier type (or operating conditions) were not conducive to attaining the effective carbon separation that has been found by other workers in the field. Certainly, it has been the experience of the present authors in various investigations that removal of coarse carbon can be effected by air classification.[1,2,17] Others have also reported the same findings. For example, Lister[21] has described an air separation system for fly ash based upon a static classifier that operates by balanced air-flow and contains no moving mechanical parts. This classifier is claimed capable of being operated to produce a "cut-point" can be selected in the range 15-100 m. The author claims:

> "The Monier Separation Technology is based upon 20 years of experience with air classification of fly ash. It has involved the development of an air classification system capable of improving fineness and particle gradation as, with a properly selected feed material, achieving a reduction in the fly ash loss on ignition."

Lister reported that classifiers such as these have been installed and operated in six power stations in Australia and the USA.

These observations suggest strongly that simple application of air classifiers commonly used in mineral processing is not an effective approach to UBC removal. Rather, it is necessary to approach the problem using different classifier parameters as it would seem was accomplished by the Monier company.[21,22]

In addition to the above reports of classifier use, a number of patents and process descriptions have been published in the area of separation of fly ash into multiple "products". Early references date from approximately 1960 when Minnick[23] claimed removal of particles >200 mesh (70%, - 325 mesh). More recent examples are briefly noted below.

The ENERCON Process[24] claims air classification of non-magnetic fly ash; other combinations of magnetic separation and air classification are included in related patents to produce products with >85%, -325 mesh for use as pozzolan.

From the perspective of ash properties, effective air classification offers a number of advantages, namely:

- Reduced coarse and mid-size particle content;
- Reduced carbon content;
- Reduced variability;

- Increases in pozzolanic activity;
- Improved concrete workability;
- Optional recovery of value added product(s); and
- Possible carbon recovery.

As with other post collection approaches to UBC reduction, it requires additional plant and may result in some solid by-product streams requiring disposal. While commercial equipment is available, previous efforts have tended to fail at the commercial scale because of poor demand for classified ash. With the growing need to offset the impact of high UBC from low-NO_x combustion, this situation may have changed and should be re-examined.

Electrostatic Separation.

Removal of carbon from ash by dry methods, other than by screening or air classification has relied largely upon the use of electrostatic separation. Electrostatic separation exploits the forces acting upon charged particles in an electrical field. In practice, three main methods are used to induce charges in particles: corona discharge, conductive induction, and contact electrification. Corona discharge and conductive induction are used to separate good conductors from poor conductors.

Corona discharge is used in the roller-drum type of electrostatic separators that are adequate for coarse particles but tend to fail as particle size decreases. The electric "wind" generated by ion bombardment from the corona, acts along with convection currents generated by the rotating drum to cause small particles to fly away from the drum and be lost and result in extensive dust production. Because of the fine particle size of fly ash, any surface dependent separator has a limited capacity because each particle must contact the surface. Consequently, the moving drum surface must move at an impractical speed to attain a significant product through-put.

Contact electrification is usually effective for separating different types of non-conducting particles. Electrification of the particles is induced by friction and is said to comprise a triboelectric charge. Such charges can be developed whenever particles collide. Subsequently, on passing the charged particles through an electric field, they will separate according to their charge / mass ratio. This phenomenon is exploited in relatively new methods of separation based upon the combination of fluidization and electrostatic fields.[25] A number of types of apparatus have been developed and patented,[26] one of which, the dilute phase electrostatic loop has been used to separate carbon from fly ash.[27] The operation of this equipment has been described by Inculet et al.[26,27] Fly ash from a bituminous coal, containing approximately 10% by mass of carbon was separated into two fractions:

- Positive electrode fraction (approx. 36% C); and

- Negative electrode fraction (approx. 2.3% C).

Subsequent processing (unspecified by the authors) was reported to have produced a carbon-rich fraction with more than 60% C. Other configurations of apparatus have been patented by Inculet[26] and Hepher.[28] In each of these patents, fly ash and carbon separations are noted.

More recently, Whitlock[29,30,31,32,33,34] has reported the commercial scale use of a triboelectric separation process by International Separations Systems, Inc. of Needham, Massachusetts. This process been demonstrated at New England Electric System's subsidiary New England Power Co's Salem Harbor and Brayton Point powerplants. Termed the UFC separator, the equipment consists of two stationary, flat parallel electrodes, charged so as to maintain an electric field between them. Between the electrodes are two sections of an open-mesh transport belt that move in opposite directions. The result is a counter-current flow of separating particles that are subjected to continued agitation, particle contact and charging. The process is claimed to be capable of handling particles in the range <5 m. to >250 m.. Applied to a range of twelve different fly ash samples from eleven stations in seven U.S. states and two countries, the UFC separator is claimed to achieve reductions in LOI (assumed to be largely due to carbon removal) ranging from 25% to over 70 percent.

The ISS system has a small capital cost compared to the FBC burnout process. The key to its success may be the market for the high-carbon fraction of ash. The current cost for high-grade activated carbon is on the order of $1-$2/lb, which is two-orders of magnitude greater than the fuel value of the carbon. If the unburned high carbon ash form the ESP could substitute for some of the sorptive applications of commercial activated carbon it could be economically attractive.

Results from a 3,000 ton production test were reported in May 1995 with an average reduction of ash feed LOI from 8.19% down to 2.26% in the low carbon product. All of the low carbon ash that was produced was claimed to have been used in concrete products.[29,30,31,32,33,34]

Carbon Flotation.

Most size-separation methods applied to fly ash are based upon differences in particle size, specific gravity, or surface chemistry. In principal, physical separation of particles exploiting these properties is more effective in wet rather than dry processing systems. In practice, the use of wet systems, in which the mass of particles to be treated is suspended in a fluid (usually water), is complex and costly. One patented approach, the AMAX process[35] includes size separation by wet screening at 200 mesh as an element in a complex flow sheet.

Overall, the use of wet separation methods can be expected to have many disadvantages when applied to coal ash, notably:

- The use of water as a separation medium results in the need for expensive water handling, settling, treatment, and discharge systems;
- The quantities of water required are large when size separation processes are involved; and
- Typically, a filter-cake of ash contains 20 to 25% of water that must be removed by drying which will involve considerable energy costs.

Clearly, it is advantageous to avoid the use of wet-processing unless the existing plant ash collection system is based on water lagooning and has the capacity to handle any additional demands introduced as part of a separation process.

Further, in the case of carbon removal, simple wet sizing (other than by screening) would not be effective because of the large density differences between the coarse carbon particles and the ash spheres. To be effective, such separation requires the "assistance" of froth flotation procedures. The process of froth flotation was first developed for mineral separation in the early 1900s. It is the dominant process in modern mineral processing and has been applied to coal, graphite and other carbon forms. In its simplified form, the process exploits differences in surface properties between the components of a ground mineral mixture: in the present case, carbon and inorganic ash particles. It consists of treating the wet ground pulp (ash) with reagents (collectors or promoters) that render some mineral surfaces hydrophobic while leaving other species hydrophilic. When air is introduced the bubbles preferentially attach to the particles with hydrophobic surfaces; these are then lifted to the surface to form a "froth" where they are stabilized by a frothing agent (frother) and can be removed by scrapers or by overflow. The unfloated residue forms a tailing in mineral processing but may be a "cleaned" product in an ash recovery system.

The choice of collectors varies widely dependent upon the mineral to be floated. Fuel oil and kerosene are both widely used for flotation of coal or graphite, since they are readily absorbed by these naturally hydrophobic materials. Common frothers are pine oil, cresylic acid, polypropylene glycol ether and 5- to 8-carbon aliphatic alcohols. For example, in the case of Fly Ash 3 (Table 6-2), processing was continued further on the -45 m. fraction and the carbon content was reduced to 0.2% by froth flotation using kerosene and MIBC.[1] This collector/frother combination was originally found successful with fly ash by Stemerowicz and Bruce.[36] Other reports of flotation using other agents are also in the published literature.[1,16,37,38]

Although flotation is technically effective, producing low LOI ash and a good carbon concentrate, it does present significant disadvantages when applied to ash, as follows:

- It has all of the general disadvantages associated with wet processing of ash;

- With a low-grade, fine-particulate "ore" such as ash, there is significant attrition of expensive flotation chemicals by absorption on the carbon-free ash product; and
- Not only are the chemicals lost, they may interfere with the use of the carbon-free ash.

Ammonia Removal

As discussed in Section 5, the selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) processes inject one of a number of nitrogen-based chemical reagents into the flue gas to react with NO_x in the presence of oxygen, forming nitrogen and water vapor. The most common reagents used are urea and ammonia (anhydrous and aqueous). Ammonia contamination of ash has negatively affected ash utilization at some locations.

Ammonia contamination of ash from NO_x reduction processes has not yet been experienced in North America. However, a number of utilities have used ammonium sulphate as a precipitator aid with the result that ash has been significantly contaminated. Such ash has been rejected by the cement and concrete market, which is now exceptionally conscious of any potential ammonia contamination in ash. Overall, this market for ash is sensitive to any problem issues.

Typical ranges of ammonia contamination from different NO_x control processes and from ESP conditioning are:

Process	NH_3 Slip (ppm)	NH_3 in Ash (mg/kg)
SCR	2-5	50-120
SNCR	5-10	250-600
ESP Conditioning	10-30	700-1200

A first step to avoiding the potential impact of ammonia contamination of ash on sensitive markets could be in the nature of an educational approach based on the reported information that in Europe contamination in the 50-120 mg/kg has been regarded as not being a problem in cement and concrete applications (see Section 5). User education may distinguish low-NO_x ash from other ashes containing ammonia at much higher concentrations.

An alternative approach would be to encourage utilities to use the simplest mitigating measure for reducing NH_3 in fly ash, namely: to conduct plant operations at a maximum ammonia slip of <2 ppm. In the event that this is not feasible or that acceptable ash cannot be produced, it may be necessary to undertake beneficiation by some form of post ash collection NH_3 stripping, as described below.

Removal of ammonia or ammonium compounds requires the application of chemical or thermal methods. Processes exist for thermal reduction of ammonia concentrations in fly ash due either to the use of "precipitator aids" or from "ammonia slip" during NO_x reduction by SNCR. According to Hjalmarsson[39], these processes were not being used at commercial plants at the time of publication (1990). However, pilot plants have operated in Germany and Japan.[39] Numerous patents relevant to ammonia removal or reduction have been published.[40,41,42,43,44,45,46,47,48,49, 50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68]

As discussed in Section 5, ammonia is deposited on fly ash in the form of ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bisulfate (NH_4HSO_4). Although the proportions of each present will vary with combustion conditions, usually both salts are present. Both of these compounds decompose on heating and both are very soluble in water. The patent literature indicates that both of these properties have been exploited and three general process types have been proposed, namely:

- Heating in air;
- Heating in the presence of steam; and
- Scrubbing or leaching with water.

A substantial number of patents have been issued or applications made for processes based on heating ash in the temperature range 300 to 500°C;[40,44,45,46,47,59,63,67] others cite higher process temperatures up to 800°C.[62] Fluidized bed or rotary kiln heating processes are often proposed, and in some cases steam may be injected to strip NH_3. Flue gases are a common source of waste heat. From the perspective of subsequent ash use in concrete, operations at the lower temperature range should be preferable, as these offer less risk of reducing ash reactivity.

Processing at lower temperatures (<250°C) is proposed by using added water and sometimes a base such as lime.[41,48,54] Patents for two processes using leaching or scrubbing were also found.[43,52] As with all ash beneficiation approaches that require wet processing, removal of NH_3 into an aqueous stream will be disadvantageous if a dry ash product is required.

In most cases an important process concern is the reuse of the regenerated NH_3 in the NO_x reduction process. [43,44,45,46,47,48,52,56,58,59,61,63,65,68]

Summary

Several options are available to upgrade ash quality for more critical markets such as cement and concrete applications. These include carbon management by combustion optimization, selective ash collection, and ash beneficiation. Beneficiation techniques to remove UBC include carbon burn-out and physical removal of carbon which could include screening, grinding, air classification, electrostatic separation, and carbon flotation. The relative merits of each of these techniques has been discussed. Most experience has come from air classification of ash, although the electrostatic technique appears to hold good promise, with the added advantage that the carbon is recovered as a usable by-product. This is not true with the burnout technique which also has the potential problem that although the ash may conform to specifications in terms of LOI, it may have lower pozzolanic reactivity due to the effect of high temperatures (annealing) on the reactive glass phases. This factor needs to be explored further. Wet techniques for ash upgrading, such as flotation, are not considered to be feasible unless coupled in some way with a wet process-an unlikely situation.

While commercial equipment is available, previous efforts to upgrade ash have tended to fail at the commercial scale because of poor demand for classified ash. With the growing need to offset the impact of high UBC from low-NO_x combustion, this situation may have changed and should be re-examined.

Techniques for removing ammonia contamination from ash have been reported in the patent literature and include heating in air, heating in the presence of steam, and scrubbing or leaching with water. None of these are particularly well suited for the processing of large volumes of relatively low value-added fly ash, unless waste heat can be used and the regenerated ammonia can be recycled back into the NO_x reduction process.

7

GLOSSARY

ACAA	American Coal Ash Association
AOFA	Advanced overfire air
ASTM	American Society for Testing and Materials
BBF	Biased burner firing
BOOS	Burner out of service
BRE	Building Research Establishment
Btu	British thermal unit
C/ANM	Coal/air nozzle modifications
CAA(A)	Clean Air Act (Amendment)
CCB	Coal combustion by-product
CCOFA	Close-coupled overfire air
CDM	Combustion design modifications
CEMs	Continuous emission monitors
COM	Combustion operations modifications
DOE	(U.S.) Department of Energy
ECE	Economic Commission for Europe
ESP	Electrostatic precipitator
FGD	Flue gas desulfurization
FGR	Flue gas recirculation/reburning

GNOCIS	Generic NO_x Control Intelligent System
GWe	Gigawatt
IFNR	In-furnace NO_x reduction
KEMA	Keuring van Electrotechnische Materialen N.V., Arnhem
lb/MBtu	Pounds per million Btu
LEA	Low Excess air
LNB	Low NO_x burners
LOI	Loss on ignition
MPa	Megapascal
MWe	Megawatt
NAAQS	National Ambient Air Quality Standards
ng/J	Nanogram per Joule
Nm	Newton meter
NO_x	Nitrogen oxides
NSPS	New Source Performance Standards
OFA	Overfire air
PETC	Pittsburgh Energy Technology Center
ppm	Parts per million
psi	Pounds per square inch
RACT	Reasonably available control technology
RAP	Reduced air preheat
RCRA	Resource Conservation and Recovery Act

SC	Staged combustion
SCR	Selective catalytic reduction
SNCR	Selective non-catalytic reduction
SOFA	Separated overfire air
UBC	Unburned carbon
w/c	Water to cement ratio

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