Ammonia Removal from Fly Ash by Carbon Burn-Out

Vincent M. Giampa
vgiampa@electricfuels.com
727-827-6647
727-824-6603 (fax)
Progress Materials, Inc.
One Progress Plaza
St. Petersburg, Florida 33701

Carbon Burn-Out (CBO) combusts residual carbon in fly ash, producing a very consistent, low carbon, high-quality pozzolan. The process is continuous and is fueled solely by the residual carbon. Heat is recovered and sent back to the power plant that originally produced the high-carbon fly ash.

Progress Materials, Inc. has developed this technology, with support from EPRI and EPRI members. Extensive concrete testing has been done in order to demonstrate the superior characteristics of very low-carbon Class F fly ash from CBO. Carbon Burn-Out's ability to consistently produce high quality pozzolanic fly ash from numerous sources has been extensively documented. CBO fly ash has gained market acceptance and is regarded as a premium fly ash product in its market area.

Fly ash from pulverized coal power plants is a valuable mineral admixture in concrete. Its performance and economy have been well documented for several decades. Among other beneficial properties, fly ash enhances concrete's durability, especially its resistance to chemical attack. High-performance concrete combines high strength with long life, and is increasingly favored by life cycle costing. Fly ash is an important ingredient in this high value concrete.

Recently several utility ash managers have expressed concern about the ramifications from the increasing number of power plants injecting ammonia into coal fired generators. Coal fired power generation facilities are under increasing regulatory requirements for NO_x emission reductions. Recent United States EPA rule changes have resulted in coal fired utilities in states east of the Mississippi with the exception of Florida, Maine and Vermont be required to meet NO_x emissions of .15 lbs./ mmBTU.

In order to meet the new NO_x emission requirement, many utilities will use a combination of combustion management and post combustion processes. Combustion management techniques include low NO_x burners, over fired air systems, reburning and flue gas recirculation. The most commonly used combustion management technique is low NO_x burners. Low NO_x burners contribute to higher residual carbon levels in fly ash especially when operating for maximum NO_x removal. Post combustion processes include SCR selective catalytic reduction and SNCR selective non catalytic reduction.

Post combustion processes, SCR and SNCR use ammonia in the conversion reaction of NO_x to nitrogen and water. SCR normally uses a metal catalyst downstream of the economizer. SCR can accommodate different reaction temperatures depending on catalyst formulation. SCR systems have been successfully used in the 350°F to 1100°F temperature range.

SNCR ammonia injection occurs in the hot zones of the boiler and uses heat to drive NO_x reduction reactions. The NO_x reduction reaction will proceed at temperatures in the 1600°F to 2100°F zone. Both SCR and SNCR reduce NO_x by the following reactions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

Post combustion NO_x controls result in a certain level of inefficiency in regards to the ammonia reducing process. This inefficiency results in fugitive ammonia emissions called ammonia slip. SCR systems typically operate with ammonia slip values in the five ppm range while SNCR systems operate considerably higher. Ammonia slip can be expected to vary widely depending on changes in operating conditions.

Ammonia slip results in a significant portion of ammonia being deposited on fly ash. European data indicates that combustion of coal in the 6–8 % ash range with slip values of 2 ppmv in the flue gas result in concentrations of approximately 100 ppmw of ammonia on fly ash. This example indicates that approximately one third of the ammonia slip reports to the fly ash.

Currently, little documentation exists as to the amount of ammonia residues found on fly ash resulting from NO_x reduction operations. It has been reported that low NO_x operations can produce ammonia concentrations in fly ash in the thousand ppm range.

NO_x control technologies will result in increased levels of carbon and ammonia found on fly ash. Carbon contents above 3% and ammonia concentrations above 100 ppm have been found to decrease fly ash market value. In fact, use of these technologies may result in once marketable fly ash becoming unusable and destined for disposal.

Ammonia contaminated fly ash will also result in re-evaluation of landfill disposal practices. Ammonia residues found on fly ash exhibit high water solubility and have the potential to contaminate both ground and suface waters.

Given the high probability of future fly ash sources containing increased carbon and ammonia, Progress Materials Inc. conducted an investigation as to ability of Carbon Burn-Out technology to simultaneously remove carbon and ammonia from fly ash.

Carbon Burn-Out has long been known as a very robust system for carbon removal for various types of ash feedstocks. Ash feedstocks containing carbon contents as high as 90% have been successfully processed. To date, over 200,000 tons of Carbon Burn-Out processed fly ash has been produced. CBO processed ash exhibits excellent pozzalanic activity, consistent air entrainment, carbon levels of 2 ½ % and has gained excellent market acceptance in it's market areas.

Carbon Burn-Out's fluid bed technology provides heat and residence time dictated by conditions for optimal combustion of carbon found in fly ash. Fly ash residence times of 45 minutes and temperatures in the 1300°F range are characteristic of the CBO process. Kinetic theory suggest that CBO conditions should be ideal for ammonia removal.

Ammonium Sulfate and Ammonium Bisulfate are the two prominent ammonia compounds found in coal fly ash. Both compounds exhibit low decomposition temperatures and should readily decompose within the operational conditions of Carbon Burn-Out.

In order to determine the effectiveness of ammonia removal by Carbon Burn-Out, several fly ash feed stocks of differing ammonia contents were processed. Processing was accomplished using Progress Material's one ton per hour pilot faciltiy located in Tampa, Florida. Fly ash was from a urea based SNCR fitted generating station. Fly ash of differing ammonia concentrations were processed.

Both feed and product samples were analyzed for ammonia content. Ammoniated fly ash was tested by several different methods. Testing methodology for ammonia in fly ash is not well defined. Presently no published methods for the determination of ammonia residues in fly ash exist. Well-defined methods have been used for solid matrices in the environmental testing industry. Environmental methods were selected for use in our testing program. Four methods were used ensuring method efficiency:

- EPA 350.2 uses aggressive acid distillation ensuring efficient ammonia recovery. A color-metric procedure is used for the determination of ammonia content.

- EPA 350.3 uses a less aggressive water dissolution for ammonia recovery. It is assumed that all ammonia complexes are highly soluble in water. A color-metric ammonia determination is used in this procedure.

- SM-4500C is a field technique designed for rapid determination of Ammonia during pilot plant operation. This method uses water dissolution followed by ammonia titration.

- The Boral procedure also provides a rapid field technique where the sample is treated by raising the pH and increasing sample temperature. The treatment results in the evolution of ammonia vapors, which are quantified by ammonia sensitive gas detector tubes.

Results indicate that under normal Carbon Burn-Out operating conditions essentially all ammonia was liberated from the fly ash feed material. Carbon Burn-Out successfully removed ammonia from feed ash containing ammonia at concentrations less than 1000 ppmw. **The Carbon Burn-Out process produced ash with less than five ppmw ammonia content for all feedstocks tested.**

Future work involves the determination of the fate of released ammonia in the flue gas. Results thus far concerning the fate of released ammonia are inconclusive. Two preliminary ammonia mass balance analyses indicate that 50 – 95% of the ammonia is being disassociated. Residence time and temperature inherent in the Carbon Burn-Out process should provide the necessary conditions for ammonia disassociation by the following reaction:

$$2NH_3 \rightarrow N_2 + 3H_2$$

Currently tests are being designed to determine the fate of the liberated ammonia.

U.S. Department of Energy
National Energy Technology Laboratory
2000 Conference on Unburned Carbon in Fly Ash
May 16, 2000

Full Scale Carbon Burn-Out and Ammonia Removal Experience

By James G. Keppeler, Vice President, Progress Materials, Inc.

Introduction

Fly ash from pulverized coal plants can be a valuable mineral admixture in concrete provided it meets quality criteria such as size consist and low carbon and ammonia content consistently. Meeting all of these parameters reliably is an expanding challenge in an increasingly complex world. Ash quality problems lead directly to increased disposal, which is beginning to look even more ominous from an environmental/regulatory perspective.

Application of low-NOx burners in recent years as a result of Clean Air Act requirements have driven residual carbon levels in fly ash higher. To the extent that the ash was already marginal in meeting customer demands for low LOI, cleanup of that ash is now needed to maintain, and even improve, the market for that ash and avoidance of disposal.

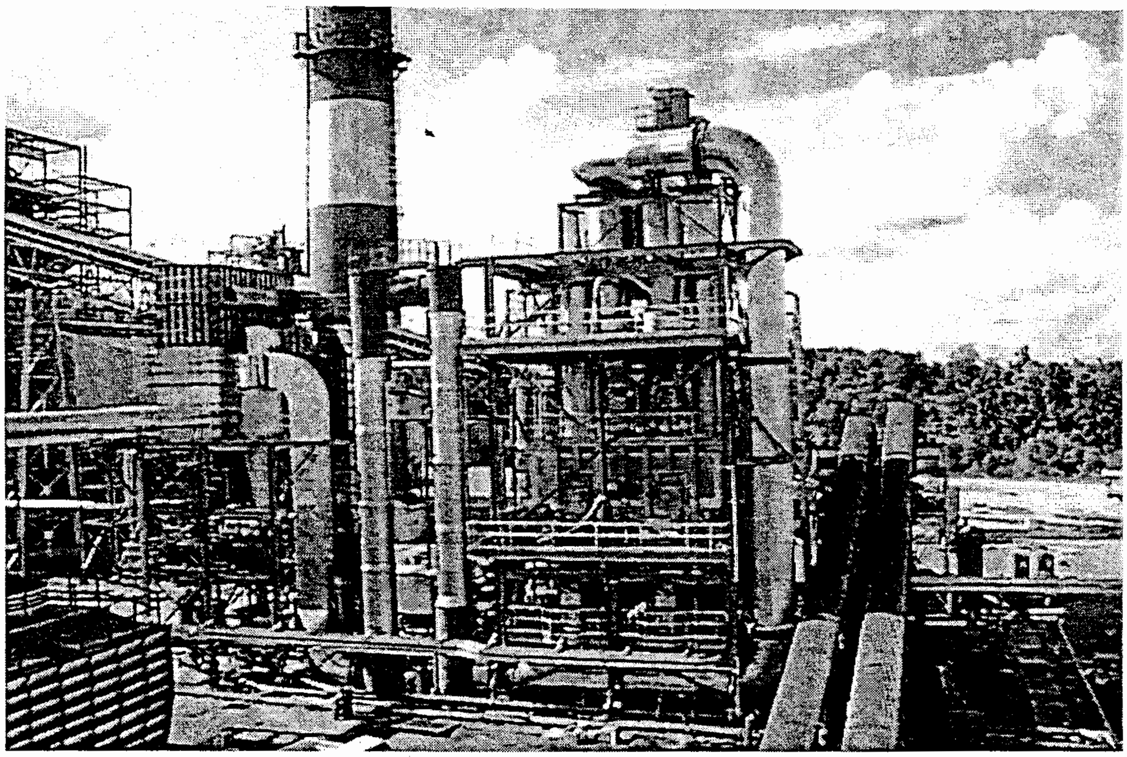
In addition, ammonia injection is used in some cases to enhance electrostatic precipitator performance, and is being applied widely in Selective Catalytic Reduction (SCR) and Selective Non-Catalytic (SNCR) Flue Gas Treatment Systems to meet more stringent NOx standards than can be met solely with low NOx burners. Ammonia contamination resulting from such systems further exacerbates the situation, and removal of ammonia is needed for any ash containing more than about 50-100 PPM (current range of limits being considered) if it is to be used in concrete applications.

Progress Materials, Inc. (PMI), a subsidiary of Florida Progress Corporation (which also holds Florida Power Corp), has long recognized the benefits of using combustion technology to transform high-carbon fly ash into a marketable product. PMI developed a proprietary technology and patented process called Carbon Burn-Out (CBO) to not only accomplish carbon reduction, but also recover the energy associated with this carbon to improve the overall power plant efficiency of the host ash source. As a side benefit, and without modification to the CBO, any ammonia on the ash is reduced to non-detectable levels.

South Carolina Electric and Gas CBO

The first full-scale application of CBO went into commercial service at the Wateree Station of South Carolina Electric and Gas in January, 1999. Wateree is a two-unit, 772 MW plant located southeast of Columbia, SC. Design basis of the CBO installation is to process 180,000 tpy of ash with an average of 12.5% LOI.

A summary overview of that installation follows:



CBO plant with Wateree stack in background

Referring to the above photo, the Fluid Bed Combustor is within the tower at right-center. The heat exchanger is the inverted "U" in the center, and the product ash/flue gas separation takes place in the tower at left-center. FD and ID fans are behind the heat exchanger, as is the condensate pump and piping system. The CBO Control Room is just off the right border.

The CBO site at Wateree Station was selected for offering minimal duct runs while maintaining open access to all existing power plant systems. The ash product storage and load-out system is about 400 feet behind the photographer.

The CBO Fluid Bed Combustor (FBC) was designed and fabricated by DB Riley, using PMI's process design parameters. The combustor is a refractory-lined steel box divided into two cells to allow precise process control. The bed consists of only fly ash. For ease of maintenance, nearly all penetrations are through the roof. A start-up burner, fired by

No. 2 oil, is in the air plenum below the bed. This burner is ramped down and then shut off once the bed reaches the residual carbon auto-ignition temperature of about 860° F.

CBO fluid bed temperature is precisely and automatically controlled by a 'recycle' system metering cooled product ash back to the FBC, where the returning product ash acts as a thermal load. The rate at which this ash is metered into the FBC is determined by the temperature profile in the fluid bed at any point in time -- increasing temperatures signal for more cool ash, declining temperatures signal for less. Pilot plant work first demonstrated this to be a very effective temperature control technique. It has the added benefit of 'smoothing out' minor variations in ash product LOI. In addition, an Exhaust Gas Recirculation (EGR) system has been added since initial operations commenced and provides significant additional control, especially for enhancing turndown capability.

Environmental permitting for the Wateree CBO project proved quite straightforward. There is no solid or liquid waste stream from the CBO process -- all incoming high-carbon ash exits as a combination of product ash and flue gas. Wateree's heat rate is materially improved, resulting in less coal combusted for a given amount of electricity produced. Therefore overall site emissions are the same or less. Fly ash disposal at Wateree is minimized.

CBO Experience to Date:

Over 18,000 tons per month of premium fly ash have been sold from the Wateree CBO. Feed ash LOI to the CBO has ranged from 6.5 to 18%, averaging 10.9%, while product ash has consistently averaged 2.5%, as targeted, and performed exceptionally well in the marketplace. It should be noted that product LOI can be lowered to a target of 2% or less if desired. However, experience with product performance on CBO ash yields most acceptable results at the current target.

Recovery of heat from CBO Wateree and application back to the turbine cycle in the power plant has functioned fully as designed.

Two people per shift perform CBO plant operations, including quality control on the product ash being shipped.

Production capacity (determined by amount of carbon combusted per unit of time) of the Wateree CBO plant is 20% greater than predicted in pilot plant testing prior to design of the full-scale unit.

The Wateree CBO fly ash has the same superior air entraining characteristics demonstrated by the bench model and pilot plant product ash, even at slightly higher LOI than observed in the preliminary testing. Hardened concrete testing confirms the good strength-producing characteristics expected of Class F fly ash. There is no significant correlation between LOI and the concrete strength results obtained to date.

The Wateree CBO fly ash product is finer in particle size than the high-carbon feed ash, and is very similar to the fineness of low carbon fly ash produced by the Wateree units before Low NO_x burners. The CBO product fly ash shows no signs of agglomeration or other detrimental properties. The fly ash has performed very well in the concrete marketplace and is viewed as a premium product.

Future Implications

Further reductions in NO_x emission limits may well require the application of either Selective Catalytic Reduction (SCR) or Selective Non-Catalytic Reduction (SNCR) technology. Both are known to deposit ammonia onto the fly ash. Even at relatively low levels, ammonia-on-ash presents significant marketing problems and perhaps occupational health and safety issues as well.

Progress Materials conducted a CBO pilot plant test program on over 25 tons of high-carbon fly ash containing several hundred parts per million of ammonia. This work demonstrated that, even without process flow changes, product ash from the Carbon Burn-Out fluid bed is both low-carbon and ammonia-free. Long residence times (particles average about 45 minutes in the fluid bed) together with average temperatures in the 1350° F range promote those reductions.

Summary

- Carbon Burn-Out has proven effective and efficient in producing a consistent, very high quality fly ash
- The plant has demonstrated its ability to produce a consistent 2.5% LOI product from a range of feedstock carbon contents and sources
- The CBO process flow was successfully enhanced so as to provide a much greater operating range than originally designed
- Plant storage and loadout features significantly enhance market flexibility
- Heat recovery back to the power plant functions fully as designed
- CBO product ash quality meets or exceeds applicable specifications and the concrete market's requirements
- Ammonia-on-ash is a now major concern. Carbon Burn-Out produces ammonia-free fly ash