Project Title

Scale-Up and Demonstration of Fly Ash Ozonation Technology

Final Technical Report
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ABSTRACT

The disposal of fly ash from the combustion of coal has become increasingly important. When the fly ash does not meet the required specification for the product or market intended, it is necessary to beneficiate it to achieve the desired quality.

This project, conducted at PPL’s Montour SES, is the first near full-scale (~10 ton/day), demonstration of ash ozonation technology. Bituminous and sub bituminous ashes, including two ash samples that contained activated carbon, were treated during the project. Results from the tests were very promising. The ashes were successfully treated with ozone, yielding concrete-suitable ash quality. Preliminary process cost estimates indicate that capital and operating costs to treat unburned carbon are competitive with other commercial ash beneficiation technologies at a fraction of the cost of lost sales and/or ash disposal costs. This is the final technical report under DOE Cooperative Agreement No.: DE-FC26-03NT41730.
ACKNOWLEDGEMENTS

Throughout this project, the authors sought direct communication and information from various companies and individuals to augment and/or confirm the available information.

Specifically, we would like to acknowledge the help and feedback from the following organizations:

- CMT Labs
- AET, Inc.
- Dairyland Power
- FL Smidth
- WEDECO
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LIST OF ACRONYMS

DOE    Department of Energy
NETL   National Energy Technology Laboratory
ESP    Electrostatic precipitator
FGD    Flue gas desulfurization
ID Fan Induced draft fan
FI     Foam Index
cfm    Cubic feet per minute
kW     Kilowatt
MW     Megawatt
O&M    Operation and Maintenance
PC     Pulverized coal
PRB    Powder River Basin
FBH    Fuller Bulk Handling Division
PPL    PPL Generation, LLC
EPRI   Electric Power Research Institute
EES    Energy and Environmental Strategies
SECTION 1. EXECUTIVE SUMMARY

Objectives

PPL lost concrete marketability for much of its ash from the Montour Steam Electric Station (SES) due to high carbon content, a common effect of low-NOx combustion measures. The objectives of this project were to demonstrate ash ozonation technology on a utility site, confirm effectiveness through a complete battery of technology performance and concrete quality tests, and if successful, to develop a basis for its implementation at the PPL Montour station and for technology transfer to other U.S. coal-fired plants.

Markets for Fly Ash as a Product

The disposal of fly ash generated from the combustion of coal has become increasingly important, as economic and environmental objectives call for recycling alternatives to traditional landfill options. Fortunately, fly ash is a desirable component in several product applications.

The most widespread and economically attractive option for utilizing fly ash is in concrete manufacture where the fly ash serves as a partial replacement for Portland cement, thereby saving cement costs, improving certain concrete properties (such as long term strength and permeability), and slowing the heat release of hydration, which can be a beneficial effect in large pours.

Fly Ash Beneficiation Techniques

For simplicity in understanding the major types of fly ash beneficiation processes and the fundamentals of how the technologies alter the quality of fly ash, beneficiation methods can be divided into two categories: 1) carbon passivation, and 2) carbon removal. In the latter case, the problem is solved by removing all or some of the carbon present in the fly ash. In the first case, the carbon is modified to behave in such a way as to mitigate its negative impacts.


Ash Ozonation - Process chemistry

Extensive laboratory work has demonstrated that the fundamental beneficial effect of ozone is caused by the formation of oxide groups on the surfaces of unburned carbon. Figure 1.1 gives an example of the laboratory data showing sharp reductions in the surfactant adsorptivity (foam index) as a function of the amount of ozone introduced to the bottom of a fixed bed of fly ash.
Normalized surfactant adsorptivity

Figure 1.1. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples. Data points represent a range of ash types, bed masses (50 - 400 gm), ozone concentrations (500 ppm - 2 vol-%), and contact times (10 - 800 min). All data are for fixed bed treatment at ambient temperature and pressure.

Project overview

PPL supplied two non-salable ashes, as well as ash handling equipment at the station (e.g. silos, fans, etc.). Ashes from other (non-Montour) sources were also be obtained and tested to evaluate the influence of different ash parameters on the effectiveness of the ozonation technology. FL Smidth’s Airmerge blender technology was used as the fluidization/ozonation vessel, with ozone being supplied by a WEDECO SMA50 ozone generator system.

A test matrix of operating conditions and carbon/ozone stoichiometries was developed and guided the parametric test program. Concrete testing of treated ash samples were performed by CMT and AET, Inc. laboratories, and supporting analyses of the ashes were carried out at the Brown University research laboratories. The project team developed preliminary engineering and cost estimates for the full-scale application of the technology at Montour SES. Test matrices and procedures are provided in section 4.

Flyashes in Test Program

Five test fly ash samples were selected for the Montour testing program, defined as follows: PPL Hard Grind, PPL Regular Grind, Dairyland JPM station fly ash, Dairyland Genoa ash and Baltimore STI ash blended with Activated Carbon. (see Figure 4.2)

PPL Hard grind is a class F representative fly ash from Montour SES, with a reported LOI under 6 %. The LOI values of untreated PPL Hard grind fly ash used in the program and measured at Brown varied slightly on a day-to-day basis from 2.3% up to 5.5 %. The
untreated PPL Hard grind fly ash was tested for LOI and AEA uptake each day before the experiment.

PPL Regular Grind fly ash is also a fly ash from Montour SES with a measured LOI range of about 3.3% to 5.5%.

Dairyland Power provided class C ash from its JPM power station, with a reported LOI approximately 0.8%. This was a typical Class C ash and exhibited yellowish color.

Dairyland also provided a second fly ash (Genoa fly ash), which is an ash resulting from the combined combustion of bituminous and sub-bituminous coals with a result typical of a class C ash yellowish color. The LOI of the untreated Genoa fly ash was measured to be 4.2% at the Brown University test laboratory.

The final fly ash in the test program was a beneficiated fly ash provided by Separation Technologies, Inc. (STI) from its Brandon Shores station ash management program (referred to in this report as STI Baltimore). This ash was used in the program as the reference class F ash for concrete test comparisons and verification. It was also used as the source for the two fly ash and AC batches (1.5% and 5% AC). The LOI of the reference STI treated fly ash was 0.85%.

**Summary Results and Conclusions**

The following is a summary of the major findings in the program

- Ashes tested - Class F, Class C, Class F+ Activated Carbon (1.5% and 5%)
- Ozonation treatment was successful on all ashes with the exception of the STI + 5% AC mix. This conclusion is based on the Foam Index results and confirmed by concrete (air entrainment) and AEA tests
- For all ashes the treatment dosage remained in the range of 0.5 to 2 lbs O3/1000lbs ash, with acceptable performance mostly under 1 lbs O3/1000lbs ash.
- Mode of fluidization (airmerge vs. simple fluid bed) seemed to have negligible impact
- O3 concentration seemed to have negligible impact on performance. Note however that O3 concentrations in the gas flow never exceeded 2% throughout the test program
- The Class F + 5% AC mix was not successfully “deactivated” by O3. At present it is not clear whether this is real limitation of the technology or simply a result of a single test with no opportunity to optimize. Future work at lab scale may help understand this better

From the conclusions and observations above, the following guidance was used for task 2 (engineering scale up and economic analyses)

- O3 Dosage: 0.5 - 1 lbs O3/1000lbs ash
- O3 concentration from generator not critical
- Contact Mode: Simple Fluidized Bed (no need for Airmerge blending features)
• Gas Flow/Velocity: Not critical based on tests results. Scale up design was based on experience between the range of MAX and MIN fluidization test results.

Sample ash buckets were retained for concrete testing at several points during the tests. These tests have confirmed the FI trends observed during the ozonation tests that indicated the successful “deactivation” of the ash. In other words, air entrainment and AEA uptake for the treated ashes have confirmed their suitability for the concrete market assessed on direct comparison with “control” or references ashes (Class F and C ashes currently being sold)

• Class F – STI Baltimore.
• Class C – Coal Creek

The test results for the STI ash “contaminated” with Activated Carbon were very encouraging as well. We can say that for the 1.5% AC sample (a high but reasonable concentration of AC possibly to be found in “real” mercury control scenarios), the ozone treatment seemed highly effective. The other sample (an extremely high 5% AC concentration likely not to be found in “real” Hg control scenarios) needs further analyses.
SECTION 2. INTRODUCTION

Objectives

PPL lost concrete marketability for much of its ash from the Montour Steam Electric Station (SES) due to high carbon content, a common effect of low-NOx combustion measures. The objectives of this project were to demonstrate ash ozonation technology on a utility site, confirm effectiveness through a complete battery of technology performance and concrete quality tests, and if successful, to develop a basis for its implementation at the PPL Montour station and for technology transfer to other U.S. coal-fired plants.

Background

 Markets for Fly Ash as a Product

The disposal of fly ash generated from the combustion of coal has become increasingly important, as economic and environmental objectives call for recycling alternatives to traditional landfill options. Fortunately, fly ash is a desirable component in several product applications. However, this “desirability” requires that, as with any other “raw” product, the fly ash maintain certain properties (or specifications), which are dictated by the ultimate product application. Simply stated, fly ash is increasingly becoming a “manufactured” or “quality controlled” product, and no longer a mere waste.

The most widespread and economically attractive option for utilizing fly ash is in concrete manufacture where the fly ash serves as a partial replacement for Portland cement, thereby saving cement costs, improving certain concrete properties (such as long term strength and permeability), and slowing the heat release of hydration, which can be a beneficial effect in large pours.

Fly Ash Properties

The properties or quality of the fly ash are dependent on many factors ranging from the type and operating characteristics of the generating unit, the type and rank of the coal and the type of air pollution control equipment. When the fly ash does not meet the required specification for the product or market intended, it may be possible and necessary to treat (or beneficiate) it to achieve the desired quality. Just as the desired final fly ash quality depends on the product or market intended, so does the choice of the beneficiation technology.

Fly ash is mostly mineral matter. Since it is this mineral matter that is typically desirable for fly ash utilization in most applications, carbon is often considered a contaminant. The most common "faults" of carbon include:

- Adding unwanted color
- Adsorbing process or product materials (e.g. water and chemicals)
- Carrying unwanted chemicals into the process (e.g. ammonia)

Since the use of fly ash as an ingredient in the manufacture of concrete is the largest and highest value beneficial use application, and carbon can cause an increase in the water demand and the required amount of air entraining admixture (AEA), the focus of most fly ash beneficiation methods to date has been to minimize the negative effects that carbon can have in concrete.

**Fly Ash Beneficiation Techniques**

For simplicity in understanding the major types of fly ash beneficiation processes and the fundamentals of how the technologies alter the quality of fly ash, beneficiation methods can be divided into two categories: 1) carbon passivation, and 2) carbon removal. In the latter case, the problem is solved by removing all or some of the carbon present in the fly ash. In the first case, the carbon is modified to behave in such a way as to mitigate its negative impacts.

Laboratory research has demonstrated that carbon in fly ash can be made passive to air entraining agents. The best approach to passivation depends somewhat on surface area and porosity characteristics of the carbon, which would be specific to each generating unit and coal. In general, carbon in fly ash is made passive by introducing a chemical (either liquid or gas) to the fly ash, which is adsorbed onto those carbon sites, otherwise competing for the AEA. By occupying these adsorption sites before exposure to an AEA, it minimizes AEA consumption. Since the actual quantity of carbon does not change, other concerns such as color are not mitigated by passivation techniques.

With carbon removal the objective is to remove carbon from the mineral in fly ash. This approach assumes that if enough carbon is removed, the bulk of the remaining fly ash will have sufficiently little carbon, such that its negative influence is minimized. Commercial variations of this approach include carbon burnout through combustion, and carbon separation through electrostatic forces.

SECTION 3. OZONATION TECHNOLOGY

DOE and EPRI-funded work at Brown University over the last several years has led to a new concept for beneficiating high-carbon ash based on surface passivation using ozone. The team at Brown discovered that oxidation of carbon surfaces suppresses the adsorption of surfactants used in air entrained concrete (air entraining admixtures), which is the most important underlying reason for carbon restrictions on fly ash intended for concrete in North America.

Extensive laboratory work has been carried out at Brown, involving a wide range of commercial ash types, ozone concentrations, and contact times. The samples have been analyzed for surfactant adsorptivity, surface chemistry, and air entrainment behavior and strength development in mortar. A set of three inter-related patents have been granted to cover this technology (US Patent 6,136,089, US Patent 6,521,037, and US Patent 6,890,507) cover various aspects including the use of ozone to treat the surfaces of activated carbon based mercury sorbents. In addition, bench- and pilot-scale experiments in fluid bed vessels have been funded by DOE and EPRI, including the construction and operation of a pilot-plant at WEDECO in West Caldwell, NJ, a leading manufacturer of large-scale ozonation equipment. Additional background has been described in detail in an EPRI Technical Report “Novel Ash Beneficiation Processes for Managing Unburned Carbon and Ammonia”, EPRI, Palo Alto, CA: 2002. 1004395.

At the outset of this project, the concept of ash benefiting by carbon surface treatment was best regarded as a new concept based on the fundamental chemistry of air entrainment. Only through large-scale demonstration and supporting laboratory / pilot-plant work can this new beneficiation concept achieve acceptance in the marketplace with the associated benefits to the environment and to the economics of coal-based power generation. Hence, this demonstration project at Montour.

Scientific and Technical Basis for Ash Ozonation

This section describes the key scientific and engineering elements of the ash ozonation process and discusses the technical and market hurdles to be overcome.

Process chemistry

Extensive laboratory work has demonstrated that the fundamental beneficial effect of ozone is caused by the formation of oxide groups on the surfaces of unburned carbon. Figure 3.1 gives an example of the laboratory data showing sharp reductions in the surfactant adsorptivity (foam index) as a function of the amount of ozone introduced to the bottom of a fixed bed of fly ash. Figure 3.2 shows that over the same range of ozone input, the unburned carbon is not significantly consumed (in fact, LOI goes up slightly due to addition of oxide layer), so burnout is not the primary mechanism.
Normalized surfactant adsorptivity

Figure 3.1. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples. Data points represent a range of ash types, bed masses (50 - 400 gm), ozone concentrations (500 ppm - 2 vol-%), and contact times (10 - 800 min). All data are for fixed bed treatment at ambient temperature and pressure.

Figure 3.2. Effect of ozonation on Loss-on-Ignition (LOI), a standard test measuring fractional sample weight loss upon air oxidation at 700 °C, often used as an approximate measure of residual combustible matter in ash. Data indicate negligible carbon consumption in these experiments.

The ash ozonation process is currently understood to be a chemical reaction with the desired reaction expressed by Eq. 1 below. Eqs. 2 and 3 are undesirable side reactions,
whose presence partly dictates the optimal contacting scheme. Reactions 2 and 3 do not
degrade carbon or ash properties, but have the potential to consume ozone unnecessarily.
Fortunately for practical application, Eq. 1 is faster than Eqs. 2 and 3, and with the proper
contacting scheme (see below), the side reactions can be minimized and high ozone
effectiveness can be achieved.

\[
\begin{align*}
C + O_3 & \rightarrow C(O) + O_2 \quad \text{(chemisorption, desired)} \\
C + O_3 & \rightarrow CO / CO_2 \quad \text{(gasification, undesired)} \\
O_3 + C(O) & \rightarrow 2O_2 + C \quad \text{(catalytic recombination, undesired)}
\end{align*}
\]

**Gas/solid contacting**

The reaction system [1-3] strongly suggests a gas/solid contacting method involving
fluidized or mechanically agitated ash beds. The laboratory experiments to date have used
fixed or fluidized beds with reasonable effectiveness in both cases, but the fixed beds suffer
from gas channeling and are difficult to scale up. As the bed height increases, the fast
chemisorption reaction [1] saturates carbon surfaces in the lower part of the bed and any
further ozone addition leads to gasification reaction [2] in the lower part of the bed,
consuming ozone with little beneficial effect. To scale up to large bed sizes, therefore, it is
highly advantageous to incorporate solids motion, which brings fresh untreated ash down
into the vicinity of the gas distributor, and prevents the prolonged (over) exposure of any part
of the bed.

Solids motion can be achieved through mechanical agitation or gas fluidization. The
project team focused on a fluidization system based on FL Smidth’s Airmerge blender
technology. This equipment, originally designed to blend two solids, accomplishes solid bed
motion with no moving parts using a gas distributor that is segmented into four quadrants
with different air flows. By increasing the air flow in one quadrant, top-to-bottom mixing of
the ash bed is accomplished, channels are broken, and the major disadvantage of the large
fixed bed is overcome. These devices have deeper beds, which will increase ozone
utilization, and have built-in dust management systems that allow their application here
without extensive custom modification. Further and equally important, the technology can
easily be operated in a simple fluidized bed mode, allowing the test program to evaluate
different fluidization approaches.
Economics and market acceptance

Preliminary estimates from laboratory results suggested that electricity costs for ozone generation were in the range of 0.8 $/ton to 1.2 $/ton. This cost is much less than the potential economic benefit of recovering ash salability, which is related to sales revenues and avoided disposal costs. These are highly region and site-specific, but can be estimated at 20 $/ton for sales in the concrete market and 30+ $/ton for disposal. An objective of the project was to provide the data necessary to estimate total costs (capital and O&M) for the technology.

Laboratory data indicate effectiveness of the ozone process on a variety of ash types (Class F, Class C; high and low-LOI,) but there are regulatory hurdles for high-carbon ashes since ozonation leaves the LOI essentially unchanged. For this reason, the following market niches seem most applicable for the technology: (1) marginal high-carbon ash streams; (2) low-LOI, high-activity ashes, many of which are class C; and (3) low carbon ashes contaminated with Activated Carbon (AC) for mercury control. There are a number of these ashes currently being produced at U.S. utilities, and they are difficult to treat by separation processes (at least without sacrificing yield) and are poor candidates for burnout processes, since they require supplemental fuel to sustain unaided combustion.
SECTION 4. PROJECT SUMMARY at PPL MONTOUR SES

Scope of Work and Task Description

The project was divided into three tasks. In Task 1, the technology was deployed and tested at PPL's Montour SES. In Task 2 technical and economic analyses were conducted for a full-scale, commercial design of the technology. Task 3 is the Final Report to DOE.

Project overview

PPL supplied two non-salable ashes, as well as ash handling equipment at the station (e.g. silos, fans, etc.). Ashes from other (non-Montour) sources were also be obtained and tested to evaluate the influence of different ash parameters on the effectiveness of the ozonation technology. FL Smidth’s Airmerge blender technology was used as the fluidization/ozonation vessel, with ozone being supplied by a WEDECO SMA50 ozone generator system. The system was integrated with existing ash handling systems at Fly Ash Storage Silo #1 at PPL's Montour SES, as illustrated in Figures 4.1 through 4.4.

A test matrix of operating conditions and carbon/ozone stoichiometries was developed and guided the parametric test program. Concrete testing of treated ash samples were performed by CMT and AET, Inc. laboratories, and supporting analyses of the ashes were carried out at the Brown University research laboratories. FL Smidth and the project team developed engineering and cost estimates for the full-scale application of the technology at Montour SES. Test matrices and procedures are provided in section 5.

Figure 4.1. Ozone generator
Figure 4.2. Ash ozonation vessel

Figure 4.3. Flow control system
Figure 4.4 - Task 1. Semi-commercial scale installation of fluidization/ozonation technology at Montour
Montour Station

The Montour Steam Electric Station (Figure 4.5), located about one mile northeast of Washingtonville, Pa., is owned by PPL Montour LLC, a subsidiary of PPL Generation LLC. Unit 1 began commercial operation in 1972 and Unit 2 came on line the following year, both with 768 megawatts of generating capacity. Montour SES burns about 3.5 million tons of eastern bituminous coal each year, producing nearly 290,000 tons of fly ash, 70,000 tons of bottom ash and 2,500 tons of coal pulverization mill rejects.

Since 1990, Montour has reduced sulfur dioxide emissions by about 10 percent, Toxic Release Inventory reportable substances by about 25 percent and nitrogen oxide emissions by more than 80 percent.

In 2000 and 2001, the plant installed new selective catalytic reduction (SCR) systems and replaced the electrostatic precipitators on Units 1 and 2. The SCRs remove about 90 percent of the remaining nitrogen oxide leaving the boiler while the upgraded precipitators will remove almost all of the plant's coal ash. More than 90 percent of the ash currently produced at the plant is processed and beneficially used as construction material instead of being disposed of as waste (Figure 4.6).
Figure 4.6. Montour Station Ash Handling System

Project Team

The project team was assembled as follows

- **Sponsors**
  - NETL
  - EPRI
  - PPL
  - Dairyland Power
- **Host Site**
  - PPL – Montour SES
- **Contractors**
  - Fluidization System – FL Smidth
    - Ozone Generator - WEDECO
  - Test Program/analyses
    - Energy and Environmental Strategies
    - Brown University
    - CMT Labs
SECTION 5. TEST PROGRAM

Test Program – General approach and test matrix

The on-site test program was started on February 22, 2005 and ended on March 21, 2005. Dedicated concrete testing and analyses of selected treated ashes continued through the end of September.

The flow chart below (figure 5.1) provides an overview of the general approach for the parametric tests intended to determine the impacts of the major operating parameters (fluidization, ozone levels, contact times, bed height, velocities). This served as a guideline to step through the initial parametric tests and ensure that the test final matrix is thorough as well as effective. Based on the lessons learned from this first batch of parametric tests, the actual test program is summarized in figure 5.2. It identifies the ash source, type of fluidization approach (Airmmerge mode vs. conventional fluid bed mode), as well as other relevant parameters (O₃ concentration, fluidization “intensity” (max vs. min fluidization).

The essence of the test program for each test condition can be summarized simply by the following key steps

- Ozonate fly ash in vessel
- Perform Foam Index tests on “grab” samples throughout each ozonation test (at ~5 to 10 minute intervals. Test ends when FI value reaches equilibrium).
- Obtain samples of treated fly ash from each test for concrete air entrainment tests (to confirm FI results and verify suitability for the concrete marketplace)

Fly Ashes in Test Program

There were five test fly ash samples selected for the Montour testing program, defined as follows: PPL Hard Grind, PPL Regular Grind, Dairyland JPM station fly ash, Dairyland Genoa ash and Baltimore STI ash blended with Activated Carbon. (see Figure 4.2)

PPL Hard grind is a class F representative fly ash from Montour SES, with a reported LOI under 6 %. The LOI values of untreated PPL Hard grind fly ash used in the program and measured at Brown varied slightly on a day-to-day basis from 2.3% up to 5.5 %. The untreated PPL Hard grind fly ash was tested for LOI and AEA uptake each day before the experiment.

PPL Regular Grind fly ash is also a fly ash from SES station with a measured LOI range of about 3.3% to 5.5 %.

Dairyland Power provided class C ash from its JPM power station, with a reported LOI approximately 0.8%. This was a typical Class C ash and exhibited yellowish color. Note that despite its low LOI content, this is a sub bituminous ash, where even low concentrations of carbon can render it unmarketable.
Figure 5.1. Initial Test Matrix Logic Flow Chart
Dairyland also provided a second fly ash (Genoa fly ash), which is an ash resulting from the combined combustion of bituminous and sub-bituminous coals with a result typical of a class C ash yellowish color. The LOI of the untreated Genoa fly ash was measured to be 4.2% at Brown University’s laboratory.

The final fly ash in the test program was a beneficiated fly ash provided by Separation Technologies, Inc. (STI) from its Brandon Shores station ash management program (referred to in this report as STI Baltimore). This ash was used in the program as the reference class F ash for concrete test comparisons and verification. It was also used as the source for the two fly ash and AC batches (1.5% and 5% AC). The LOI of the reference STI treated fly ash was 0.85%.

<table>
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<th>Test #</th>
<th>Sample</th>
<th>Test Description</th>
<th>[O3] at generator %</th>
<th>O3 Flow SCFM</th>
<th>Total Flow SCFM</th>
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<td>12</td>
</tr>
</tbody>
</table>

Figure 5.2. Final Test Program Matrix

**EXPERIMENTAL PROCEDURES**

**Loss-On-Ignition (LOI) Test**

The carbon contents of ozonated and non-ozonated fly ash samples were determined using Loss-On-Ignition (LOI) test. The LOI values were defined using a modified standard ASTM method (Standard No. C 311-96a and C 114-94). The standard ASTM C 311-96a and C 114-94 methods involve simple procedures described below.

The LOI is calculated as the percentage weight loss from a dried, roughly one-gram sample of ash, after an initial determination of the moisture content of the as-received moist
sample. The combustion of the dried sample to a constant weight in an uncovered porcelain crucible at 750 ± 50°C allows calculation of the percentage loss on ignition, as

- **(15.69,397.39),(40.29,407.39)**

\[
\text{LOI, } [%] = \frac{\text{Mass loss from dried sample}}{\text{Mass of dried sample}} \times 100
\]

**Foam Index Test**

The foam index test permits a quick characterization of the suitability of a particular fly ash as a concrete additive.

The test involves determining how much of a particular Air Entraining Admixture (AEA) must be added to a "standardized" hypothetical concrete mix, in order to obtain acceptable air void formation in the mix. In actuality, the test mix is very dilute, in comparison to a real concrete mix. What is examined, as opposed to the air void volume, is the ability of the dilute mix to hold bubbles on its surface. The test itself gives a quantitative result, reported as the foam index value. It should, however, be recognized that this is only a qualitative guide to the problem of AEA adsorption in an actual concrete mix.

There are many factors that can influence the foam index results. Among them are the time that the mix is allowed to sit, the proportions of the different components, and the type of AEA and even its age. The test is also sensitive to user technique (how vigorously the vial is shaken, what qualitative endpoint criterion is employed). For this reason, there is no standardized foam index test. There are many similar procedures in use in various laboratories throughout the world. It is thus, inappropriate to compare the quantitative results obtained in one laboratory with those obtained in another. All foam index tests for the Montour test program were conducted by the same laboratory technician.

Foam index measurements involve placing the mixtures for testing, which consist of 2 grams of fly ash, 8 grams of Portland cement and 25 ml of distilled or de-ionized water, into a 70 ml cylindrical jar with a 40 mm I.D., 80mm length. The jar is then capped and thoroughly shaken for one minute to completely wet the cement and fly ash. In the present work, a 10 vol-% aqueous solution of either Darex II™ or Air 40 was used as the AEA in the test. The 10 vol-% aqueous solution of AEA is added one drop at a time from a pipette gun with a 0.75 ml tube. The size of the drop is adjustable, and this is done on the basis of the expected value of the foam index. After each addition the jar is capped and shaken approximately 15 seconds, after which the lid is removed and liquid surface observed. Before the endpoint of the test, the foam on the liquid surface is unstable and breaks in the matter of a few seconds. The endpoint is taken to occur when stable foam is established on the surface for at least 45 seconds. It is believed that the stable foam endpoint occurs at a relatively constant aqueous concentration of surfactant. To the extent that differing amounts of AEA must be added to the solution in order to achieve this particular concentration, this reflects different amounts of AEA being adsorbed onto the surfaces of the solids in the mixture. This is why the foam index is a measure of adsorption.

The entire procedure is repeated as above, using just 8 grams of cement and no fly ash. Subtraction of the two test results (the value for the sample with fly ash, less the value for the sample without fly ash) gives the reported foam index value for the fly ash.
In this study, the foam index tests were carried out at least twice for all samples. Those that showed good agreement between the two results were reported as a simple average of the two tests. Otherwise an additional test was performed and the final foam index was calculated as the average of the three tests.

Foam indices for different fly ashes varied over a quite significant range. The lower the foam index value, the greater the uncertainty in its value. This is partly attributable to the drop-wise incremental titration involved in the test. For a sample with a low AEA capacity, addition of one drop can significantly overshoot the true endpoint of the test. At the same time, the lower foam index samples tend also to be those with quite low LOI values. The main factor determining foam index is the LOI of the sample, since as discussed above, it is the carbon that tends to adsorb the AEA. Low LOI samples also exhibit a larger uncertainty in the LOI values themselves. Nevertheless, reproducibility was quite good in the foam index tests themselves.

Concrete testing of ozonated and non-ozonated fly ash samples

CMT concrete test procedure for class F ashes

The concept of treating fly ash or the carbon in fly ash, is to make the carbon unavailable to AEA. The purpose of these trial batches is to determine if the ozone treated carbon particle can withstand the rigorous treatment or abrasion to which it would be subjected in a concrete mixer truck.

Since ASTM C94, The Standard Specification for Ready-Mixed Concrete dictates limits of both time and mixing drum revolutions, the laboratory trial batches were subjected to similar treatment: 300 revolutions maximum and up to 1.5 hours of time prior to discharge.

The trial batches were performed using mixes with 100% Portland Cement, Portland Cement + an ash of acceptable quality, currently being used by ready-mix concrete producers in the market place, and mixes using both treated and untreated fly ash. In order to duplicate the time and mixing revolution of a truck mixer, a lab mixer was used. The lab mixer was started and stopped periodically to achieve 300 revolutions at the end of a mixing period of approximately 80 minutes. During the "rest" period between mixing cycles the concrete was tested for slump and air content.

The end result is a time vs. air content curve. If the ozone treatment is to be considered effective, being able to withstanding mixing action, it should have a similar AEA demand and air loss as the control mixes.

Laboratory trial batches were made with locally available cement, aggregates and admixtures. Both treated and untreated fly ashes were used.

All batches were prepared as per ASTM C192, “Std. Practice for Making and Curing Concrete Test Specimens in the Laboratory”. An extended time and extra mixing revolutions were added to the standard C192 laboratory procedure to simulate the maximum reasonable
hauling time of 1 to 1.5 hours and the maximum revolutions (300) allowed by ASTM C94 Std. Specification for Ready-Mixed Concrete.

The procedure of extended mixing and periodic air content testing is not a standard test but is being used to simulate the abrasive environment that a concrete mix constituent would be subjected to in a ready-mixed concrete batch plant or mixer truck.

Trail batches were mixed to produce initial slump and air contents above the design mix target of 5” slump and 6.0% air content, similar to ready-mix concrete practice.

**American Engineering Testing, Inc concrete test procedure for Class C ashes**

One cubic foot size of concrete batch was prepared with each fly ash sample in the American Engineering Testing procedure. The batches were prepared according to the procedure outlined in ASTM C192. After mixing, the concrete mix air content was monitored over the time according to the pressure method ASTM C23 “Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method.” The air content was recorded up to 90 minutes.
SECTION 6. RESULTS AND DISCUSSION

Figure 6.1 provides additional information relative to the actual test conditions observed for each test. The following definitions apply to the parameters shown in the table:

- **Sample** – fly ash source as described in section 5
- **Test description** – operating mode of the ozonation vessel
  - “Airmerge” refers to the operation of the vessel in the blending mode (varying flows to each quadrant of the vessel)
  - “Fluidized” refers to an operating mode simulating simple fluidization (uniform flow across the total fly ash bed)
  - “Max and Min” refer to the total flow to the bed (shown in the last column)
- **LOI** – LOI value for fly ash test batch
- **O3 (at generator)** – O3 concentration in the gas stream at ozone generator outlet (depending on the test condition this value is equal to or larger than the ozone concentration at the ash bed in the ozonation vessel)
- **O3 (in bed)** – O3 concentration in the gas stream at the fly ash bed (depending on the test condition this value is equal to or lower than the ozone concentration at ozone generator outlet)
- **O3 Flow** – total flow at ozone generator outlet (depending on the test condition this value is equal to or lower than the total flow at the ash bed in the ozonation vessel)
- **Total Flow** – total gas flow at the fly ash bed in the ozonation vessel (depending on the test condition this value is equal to or higher than the flow at the ozone generator outlet)

Please refer to the Appendix for the individual test results.
Summary data plots with some of the most important results are presented below. As stated previously, the initial parametric tests were designed to provide information about the impact of key physical ozonation operating parameters such as type of ozone/ash mixing (airmerge vs. simple fluidization) and gas flow rate (or velocity) on the effectiveness of the ozone/ash reactions.

Figure 6.2 shows the impact of fluidization flow rate or velocity on the resulting Foam Index to be negligible. This indicated that the fluidization velocity plays only a secondary role in the effectiveness of ozonation treatment of the ash. The relevance of this result is that effective ash/ozone contact is achieved at the lowest fluidization velocity, hence minimizing the requirement for gas flow rates.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Sample</th>
<th>Test Description</th>
<th>LOI %</th>
<th>[O3] % at generator</th>
<th>[O3] % in bed</th>
<th>O3 Flow SCFM</th>
<th>Total Flow SCFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPL Hard Grind Ash</td>
<td>Max Airmmerge</td>
<td>4.7</td>
<td>2.0</td>
<td>2.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>PPL Hard Grind Ash</td>
<td>Min Airmmerge</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>PPL Hard Grind Ash</td>
<td>Max Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>PPL Hard Grind Ash</td>
<td>Min Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>PPL Hard Grind Ash</td>
<td>Max Fluidized</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>PPL Hard Grind Ash</td>
<td>Min Airmmerge</td>
<td>2.0</td>
<td>0.8</td>
<td>0.8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>PPL Hard Grind Ash</td>
<td>Max Fluidized</td>
<td>2.5</td>
<td>0.5</td>
<td>0.5</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>PPL Hard Grind Ash</td>
<td>Max Fluidized</td>
<td>3</td>
<td>2.0</td>
<td>2.0</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>PPL Reg Grind Ash</td>
<td>Max Fluidized</td>
<td>3.2</td>
<td>2.0</td>
<td>0.7</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>PPL Reg Grind Ash</td>
<td>Min Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>PPL Reg Grind Ash</td>
<td>Max Airmmerge</td>
<td>4.2</td>
<td>2.0</td>
<td>0.7</td>
<td>12</td>
<td>35</td>
</tr>
<tr>
<td>12</td>
<td>Dairyland, Class C</td>
<td>Max Airmmerge</td>
<td>0.8</td>
<td>2.0</td>
<td>0.5</td>
<td>18</td>
<td>70</td>
</tr>
<tr>
<td>13</td>
<td>PPL Reg Grind Ash</td>
<td>Max Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>14</td>
<td>Dairyland Genoa</td>
<td>Max Fluidized</td>
<td>4.2</td>
<td>2.0</td>
<td>1.2</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>15</td>
<td>Dairyland Genoa</td>
<td>Max Airmmerge</td>
<td>4.2</td>
<td>2.0</td>
<td>1.2</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>16</td>
<td>Dairyland Genoa</td>
<td>Min Fluidized</td>
<td>4.2</td>
<td>2.0</td>
<td>1.6</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>17</td>
<td>5% AC &amp; ST Ash</td>
<td>Max Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>18</td>
<td>1.5% AC &amp; STI Ash</td>
<td>Max Fluidized</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
Figure 6.2. Parametric ozonation tests – effect of fluidization flow rate/velocity

Figure 6.3. Parametric ozonation tests – effect of different fluidization modes (airmerge vs. simple fluidization)
Figure 6.3 shows the impact of the type of fluidization (Airmerge blender vs. fluidized bed) on the effectiveness of ozonation. In this case, the impact is negligible as well. This result was significant in that it suggested that a simple fluid bed design should suffice in promoting good ash/ozone contact and that more complex/costly designs such as the Airmerge blending system may not be necessary in future applications of the technology.

Ozonation and Concrete Test Results

The table in figure 6.4 below summarizes the results of all the tests in the test matrix including Foam Index and concrete performance (air entrainment) tests. As already stated, the FI test is an indicator of how a particular ash will behave in concrete with respect to its air entrainment performance. While manufacturers often rely on the FI successfully, there is a need to validate such results. As described in section 4, air entrainment tests were conducted to provide such validation in this program. AEA uptake was also determined for several of the ashes. AEA uptake indicates the amount of AEA required for the mix, hence an indicator of chemical costs.

<table>
<thead>
<tr>
<th>Test #</th>
<th>Sample</th>
<th>LOI</th>
<th>Foam Index Untreated Ash</th>
<th>Foam Index Ozonated Ash (and test)</th>
<th>% AEA Untreated ash divided by</th>
<th>% Air at end of test</th>
<th>Air Loss rate % per 90 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PPL Hard Grind Ash</td>
<td>5.2</td>
<td>0.16</td>
<td>0.04</td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>PPL Hard Grind Ash</td>
<td>0.7</td>
<td>0.07</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>PPL Hard Grind Ash</td>
<td>0.1</td>
<td>0.02</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PPL Hard Grind Ash</td>
<td>0.11</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>PPL Hard Grind Ash</td>
<td>0.11</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PPL Hard Grind Ash</td>
<td>0.09</td>
<td>0.01</td>
<td>240</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>PPL Hard Grind Ash</td>
<td>2.5</td>
<td>0.09</td>
<td>0.03</td>
<td>240</td>
<td>4.6</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>PPL Hard Grind Ash</td>
<td>3</td>
<td>0.1</td>
<td>0.03</td>
<td>280</td>
<td>4.1</td>
<td>2.9</td>
</tr>
<tr>
<td>9</td>
<td>PPL Reg Grind Ash</td>
<td>3.2</td>
<td>0.14</td>
<td>0.05</td>
<td>240</td>
<td>3.9</td>
<td>4.1</td>
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<tr>
<td>10</td>
<td>PPL Reg Grind Ash</td>
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<td>0.04</td>
<td></td>
<td></td>
<td>4.4</td>
<td>2.2</td>
</tr>
<tr>
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<td>PPL Reg Grind Ash</td>
<td>4.2</td>
<td>0.14</td>
<td>0.04</td>
<td>500</td>
<td>3.1</td>
<td>3.1</td>
</tr>
<tr>
<td>12</td>
<td>Dairylnd, Class C</td>
<td>0.8</td>
<td>0.08</td>
<td>0.02</td>
<td></td>
<td>5.7</td>
<td>1.3</td>
</tr>
<tr>
<td>13</td>
<td>PPL Reg Grind Ash</td>
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<td>0.03</td>
<td></td>
<td></td>
<td>4.8</td>
<td>3.7</td>
</tr>
<tr>
<td>14</td>
<td>Dairylnd Grnea</td>
<td>4.2</td>
<td>0.24</td>
<td>0.06</td>
<td></td>
<td>5.1</td>
<td>1.1</td>
</tr>
<tr>
<td>15</td>
<td>Dairylnd Grnea</td>
<td>4.2</td>
<td>0.2</td>
<td>0.02</td>
<td></td>
<td>3.7</td>
<td>1.8</td>
</tr>
<tr>
<td>16</td>
<td>Dairylnd Grnea</td>
<td>4.2</td>
<td>0.18</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1.5% AC &amp; STI Ash</td>
<td>0.9</td>
<td>0.9</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1.5% AC &amp; STI Ash</td>
<td>0.95</td>
<td>0.04</td>
<td>500</td>
<td></td>
<td>3.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

CONTROL ASH

Class F Baltimore STI 0.9 0.02 180 3.2 3.2
Class F Baltimore STI 0.9 0.02 220 4.8 3.3
Class C Coal Creek 0.5 0.02

Figure 6.4. Ozonation test results summary. Foam Index, %AEA and air entrainment
Acceptability of fly ash to concrete manufactures is a function of various criteria, including such parameters as LOI, AEA uptake and air entrainment performance. While LOI must adhere to ASTM C 618 (<6%), other parameters can vary among different manufactures and ash types. For this reason, FI results were complemented with %AEA (Class F ashes) and % air entrainment (Classes F and C ashes). Finally and most importantly, “control ashes” from current, market-accepted suppliers, were used as references against which, the ozonated ashes were compared.

From the table above, the following observations can be drawn:

- The Foam Index results indicate that for all but one test (see exception below), the ozonation process was successful in effectively lowering the FI to very low values (comparable to the control ashes)
  - The exception to the above was test #17 (STI + 5% AC). This test indicated that at an ozone treatment of up to 2lbs O3/1000 lbs ash is not sufficient to “passivate” such a large quantity of AC. Due to test constraints it was not possible to test higher ozone dosages
- AEA uptake for a particular ash is reasonably related to its LOI content (see Figure 6.5). Most relevant from this table is the fact that ozone treatment was effective in lowering the untreated ashes with initially high % AEA (test #s 1, 11, 18), to values comparable to the control STI ash. (Only the Class C ashes were tested for % AEA. Dairyland Power, the supplier of the Class C ashes, and its test laboratory, AET, Inc. use air entrainment performance as the relevant reference for ash acceptability)
The % Air columns in the table refer to the amount or air entrainment at the end of the mix test (90 minutes) and the % air loss during those same 90 minutes. Various guidelines have been suggested as important to different manufactures. For example, % air entrainment should no less than 5% at the end of the test mix, or % air loss (from beginning to end) no more than about 2%. Yet, as can be seen from the Class F reference ash, neither of these guidelines applies strictly to an ash that is currently marketed successfully in the east coast. Based on these comparisons, the ozonated ashes compared favorably with the reference ashes, validating the initial FI results that ozonation was effective in passivating various ash types (including ash contaminated with up to 1.5% AC).

**Air Entrainment Test Results**

The concrete mix air entrainment test results are plotted below for the various treated ashes tested

**Class F ashes**

*PPL Regular Grind Ash*
Figure 6.6. PPL regular grind ash concrete test results – test #9

Figure 6.7. PPL regular grind ash concrete test results – test #11
Figures 6.6 and 6.7 represent PPL regular grind ash ozonated to two different levels of ozone, 0.85 and 1.8 lbs O3/1000lbs ash respectively, and compared to the Class C reference ash, as well as a pre-treated sample of the ash. In both cases, it is apparent that the ozonated ash compares well, from an air entrainment criterion, with the reference ash, particularly the ash in Figure 5.7, which has an air entrainment very similar to the reference ash. Further, it should be noted that the untreated ash in Figure 5.6 is a marginal ash that could possibly be marketed without treatment, as its untreated air entrainment profile is also quite similar to the reference ash. This is not necessarily surprising as the untreated ash had an LOI value of only 3.2% making it potentially acceptable to the concrete market.

![PPL Hard Grind Ash](image)

**Figure 6.8. PPL hard grind ash concrete test results – test #8**

Figure 6.8 present results from two ozone dosage (0.35 and 0.6 lbs O3/1000lbs ash) test conditions for the PPL hard grind ash. On the graph, the untreated hard grind ash and the Class F reference ash are also plotted. The following observations can be made...
- no significant difference between 0.35 and 0.6 O3/1000 lbs ozone treatment levels in concrete performance (i.e. the two ozone treatment levels give similar results in the air entrainment test)
- % air loss for the treated ash and the reference ash were very similar (~2.5%), while the untreated ash showed a total loss of about 3.5%

Figure 6.9. PPL hard grind ash concrete test results – test #7

Figure 6.9 is also for PPL hard grind ash. However, the ozone concentration level in the gas stream was reduced to 0.5% from the 2% in Figure 6.8. Further, the ozone/ash ratio is 0.25 O3/1000lbs ash. The data indicates that the air entrainment curve for the treated ash compares favorably to the reference ash (total loss of 3% versus 3.2% for the control ash). In addition, the untreated ash clearly shows its air entrainment deficit with a total loss of over 5%. This result also suggests that the ozone concentration in the gas flow has only a secondary impact on the effectiveness of the treatment. In other words, the low O3 concentration in this test did not preclude the adequate passivation of the ash, even at also low O3/ash ratio of 0.25 O3/1000lbs ash.
Class C ashes

Dairyland JPM ash

Figure 6.10. Dairyland JPM class C ash concrete test results – test #12

Figure 6.11. Dairyland Genoa Class C/F blend ash concrete test results – test #14
Figures 6.10 and 6.11 are indicative of the effectiveness of ozonation on Class C ashes. In both cases it is clearly shown that the untreated ashes are not suitable for the concrete marketplace, with batch air losses of about 4% and 5%. The treated ashes were all within total air loss of less than 2%. These tests were conducted for ozone/ash ratios from about 0.5 to 2 O3/1000lbs ash, without a significant difference in ultimate air entrainment performance.

Ash with Activated Carbon

Two tests were conducted with a class F ash mixed with AC (1.5% and 5%). As stated previously, the 5% AC test did not yield satisfactory FI results and was not tested for air entrainment in a concrete mix. This high AC concentration was intended as an upper limit test, not necessarily representative of expected AC levels in fly ash as a result of mercury control strategies. The 1.5% AC mix is presented in Figure 6.12 below.

Figure 6.12. Class F (STI Baltimore) mixed with 1.5% Activated Carbon concrete test results – test#18
The graph indicates effective ozonation of the ash/AC mix. The reference ash and the
treated mix exhibit essentially the same air entrainment behavior. Conversely, the addition of
the 1.5% AC to the reference ash, without treatment, clearly renders the reference ash
unmarketable, increasing the batch air loss from about 3% to over 4.5%.

Summary Conclusions

Foam Index (FI) results for all the tests at the Montour SES, as well as concrete air
entrainment and AEA uptake tests have been reviewed. The following summarizes the data
assessment at the present time.

- Ashes tested - Class F, Class C, Class F+ Activated Carbon (1.5% and 5%)
- Ozonation treatment was successful on all ashes with the exception of the STI +
5% AC mix. This conclusion is based on the Foam Index results and confirmed by
concrete (air entrainment) and AEA tests
- For all ashes the treatment dosage remained in the range of 0.5 to 2 lbs O3/1000lbs
ash, with acceptable performance mostly under 1lbs O3/1000lbs ash.
- Mode of fluidization (airmerge vs. simple fluid bed) seemed to have negligible
impact
- O3 concentration seemed to have negligible impact on performance. Note however
that O3 concentrations in the gas flow never exceeded 2% throughout the test
program
- The Class F + 5% AC mix was not successfully “deactivated” by O3. At present it
is not clear whether this is real limitation of the technology or simply a result of a
single test with no opportunity to optimize. Future work at lab scale may help
understand this better

From the conclusions and observations above, the following guidance was used for task
2 (engineering scale up and economic analyses)

- O3 Dosage: 0.5 -1 lbs O3/1000lbs ash
- O3 concentration from generator not critical
- Contact Mode: Simple Fluidized Bed (no need for Airmerge blending features)
- Gas Flow/Velocity: Not critical based on tests results. Scale up design to be based
on experience between the range of MAX and MIN fluidization test results.

Sample ash buckets were retained for concrete testing at several points during the tests.
These tests have confirmed the FI trends observed during the ozonation tests that indicated
the successful “deactivation” of the ash. In other words, air entrainment and AEA uptake for
the treated ashes have confirmed their suitability for the concrete market sassed on direct
comparison with “control” or references ashes (Class F and C ashes currently being sold)
• Class F – STI Baltimore.
• Class C – Coal Creek

The test results for the STI ash “contaminated” with Activated Carbon were very encouraging as well. We can say that for the 1.5% AC sample (a high but reasonable concentration of AC possibly to be found in “real” mercury control scenarios), the ozone treatment seemed highly effective. The other sample (an extremely high 5% AC concentration likely not to be found in “real” Hg control scenarios) needs further analyses.
SECTION 7. BUDGETARY COST ESTIMATE

In the previous sections, the technical components and results of the ash ozonation demonstration project were described and discussed. In this section, a brief cost analyses is provided to address the economic feasibility of the technology for coal fired plant applications in the US. This should not be construed as a detailed engineering level analysis, but rather a budgetary exercise based on some site-specific considerations at the Montour SES, as well as performance parameters determine during this demonstration project.

Further and equally important, is the fact that all ash beneficiation technologies share many similar Balance-of-Plant (BOP) costs. Hence, at this budgetary level estimate, one must recognize that when comparing to other competing technologies, it is necessary to differentiate the inherent costs of the technology “black box”, from the overall “project” cost, which is always site-, conditions- and objectives-specific.

From the previous section, the following key conclusions affecting critical parameters for the cost analyses, are repeated below:

- For all ashes, the treatment dosage remained in the range of 0.5 to 2 lbs O3/1000lbs ash, with acceptable performance mostly under 1 lb O3/1000lbs ash.
- Mode of fluidization (airmerge vs. simple fluid bed) seemed to have negligible impact
- O3 concentration seemed to have negligible impact on performance. Note however that O3 concentrations in the gas flow never exceeded 2% throughout the test program

From the conclusions and observations above, the following guidance was used for the engineering scale up and economic analyses

- O3 Dosage: 0.5 - 1 lbs O3/1000lbs ash
- O3 concentration from generator not critical
- Contact Mode: Simple Fluidized Bed (no need for Airmerge blending features)
- Gas Flow/Velocity: Not critical based on tests results. Scale up design should be based on experience between the range of MAX and MIN fluidization test results.

In addition to these technology operational and design recommendations, the scale up criteria was predicated on Montour SES ash management considerations. The resulting technology design package can be summarized as follows.

- Total ozonation system capacity: 27.5 tons/hour
- Number of ozonation vessels: 2
- Number of air-driven ozone generators: 2 (~1000lbs/day nominal)
• Feed and storage silos: existing
• Load-out silo: new (75 ton)

PROCESS SUMMARY

Fly ash from the precipitator hoppers is pneumatically conveyed via existing means to two existing ash silos. Ash from Silo #2 will become the feed ash for the ozonation process. Silo #1 will become the primary destination for treated ash, for storage and loading into trucks. The system is designed to process 220 tons of ash per 8-hour shift.

A new material feed valve and a Fuller-Kinyon pump will be located on the Silo #2 unloading floor to move ash into a pneumatic pipeline. A positive-displacement blower will supply conveying air.

Ash is then conveyed to one of the two ozonation vessels that act to enhance gas-solid uniformity. Ozone is added at this time. While one vessel is processing ash, the other is being drained and refilled so that the ozonation equipment is utilized to the greatest extent possible. Off-gases from the blending process are filtered to remove solids and routed to catalytic ozone-destruction units located near the ozone generators.

Treated ash drains into another Fuller-Kinyon pump located under the two vessels. Processed ash can be sent either to Silo #1 for storage or diverted to a new 75-ton load out bin located near the Blenders, which will be used when the product Silo #1 is unavailable for receipt and loadout of processed ash.

The process uses parallel, identical Ozone Generator trains that nominally produce 1000 lb/day of ozone from compressed air. The compressor and air filtering equipment also supply the ozonation process with instrument air. The ozonation equipment is located in a separate building, requiring approximately a 50-ft by 60-ft site adjacent to the load out tower.

Budgetary Capital Cost Estimate

Capital Cost

The budgetary estimate was developed by FL Smidth and PPL. Budgetary capital costs are summarized in Figure 7.1.
<table>
<thead>
<tr>
<th>Equipment and Budgetary Costs</th>
<th>Cost, $k</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLS Equipment and Services</td>
<td></td>
</tr>
<tr>
<td>Engineering</td>
<td>400</td>
</tr>
<tr>
<td>Ozone Generation and Destruction</td>
<td>1,800</td>
</tr>
<tr>
<td>Ash Filling, Blending, Filtration</td>
<td>450</td>
</tr>
<tr>
<td>Ash Conveying</td>
<td>200</td>
</tr>
<tr>
<td>Bin and Load Out</td>
<td>275</td>
</tr>
<tr>
<td>FLS Total</td>
<td>3,125</td>
</tr>
<tr>
<td>PPL Equipment</td>
<td></td>
</tr>
<tr>
<td>Ash Conveyor Piping and Fittings</td>
<td>275</td>
</tr>
<tr>
<td>Air Compressor Piping, Ductwork, Hand Valves</td>
<td></td>
</tr>
<tr>
<td>Ozone System Piping and Hand Valves</td>
<td></td>
</tr>
<tr>
<td>Water Drain Piping</td>
<td></td>
</tr>
<tr>
<td>Ozone Generation Building (OGB)</td>
<td></td>
</tr>
<tr>
<td>Heating System for OGB</td>
<td></td>
</tr>
<tr>
<td>Pipe Hangers and Stanchions</td>
<td></td>
</tr>
<tr>
<td>Structural Steel Tower for Blenders and Load Out</td>
<td></td>
</tr>
<tr>
<td>PPL Installation Services</td>
<td>775</td>
</tr>
<tr>
<td>Install Ozone Generation System</td>
<td></td>
</tr>
<tr>
<td>Other Mechanical Installation</td>
<td></td>
</tr>
<tr>
<td>Electrical and Controls Installation</td>
<td></td>
</tr>
<tr>
<td>PPL Total</td>
<td>1,050</td>
</tr>
<tr>
<td>Shipping</td>
<td>80</td>
</tr>
<tr>
<td>Contingency (10%)</td>
<td>425</td>
</tr>
<tr>
<td><strong>Total Estimated Equipment Cost</strong></td>
<td>4,680</td>
</tr>
</tbody>
</table>

Figure 7.1. Budgetary Capital Cost Estimate
Operating costs

Operating costs for the technology are dominated by the power required to run the compressors, blowers, and ozone generators. Manpower costs are estimated to be relatively modest at only about 1 FTE at Montour SES. This will be a function of other plant equipment and personnel considerations and will be site-specific.

Table 7.2 summarizes the energy requirements for the technology.

**Figure 7.2. System energy consumption summary**

**Process cost summary**

As shown above, the system design for Montour has a maximum (three shifts) ash processing capacity of 660 tons/day and approximately 1000 lb/day of ozone. In this analysis, the following assumptions are used for purposes of estimating the cost of ash treatment with ozonation technology.
• Total hours of operation/year: 5,000 (2 shifts, 85% CF) – 7,500 (3 shifts, 85% CF)
• Nominal range of ash processed: 135,000 tpy – 205,000 tpy
• Cost of electricity on site: $0.85/kwhr (note that in the table below, electricity costs were calculated based on a typical average of $0.05/kwhr)
• Annualized capital cost: 10%
• Manpower cost: $100,000/year

Using these parameters, yields the results summarized in Figure 7.3

<table>
<thead>
<tr>
<th>ASH PROCESSED RANGE (TPY)</th>
<th>ENERGY COST RANGE ($/YR)</th>
<th>CAPITAL COST RANGE ($/YR)</th>
<th>LABOR COST RANGE ($/YR)</th>
<th>TOTAL COST RANGE ($/YR)</th>
<th>TOTAL COST RANGE ($/TON)</th>
</tr>
</thead>
<tbody>
<tr>
<td>135K – 205K</td>
<td>225K – 340K</td>
<td>468K</td>
<td>100K</td>
<td>703K – 908K</td>
<td>4.5 – 5.2</td>
</tr>
</tbody>
</table>

Figure 7.3. Summary of Ozonation Technology Costs

The range of $4.5 - $5/ton seems compatible with previous preliminary assessments. Figure 7.4 taken from a recent study conducted by EPRI (“Beneficiation of Fly Ash Containing Mercury and Carbon”, EPRI, Palo Alto, CA: 2005. 1004267), provides a comparison for various ash beneficiation technologies and indicates that technologies such as the current technology, can be competitive in many instances.

An additional point to be emphasized is that the technology has the potential for further cost improvements, particularly with respect to the capital requirements. While the current work was conducted using a dedicated ozonation vessel, the results suggest that it may be possible to achieve adequate ash-ozone contact, using existing ash storage/conveying equipment. This needs to be demonstrated further, but based on the results of the various modes of ash-ozone contacting (simple fluidization vs. blender) tested, it may be worth considering in site-specific applications, especially when existing equipment lends itself to the direct injection of the ozone gas stream.
<table>
<thead>
<tr>
<th>Technology Basis</th>
<th>Number of Output Products</th>
<th>Primary Product (Low Carbon)</th>
<th>Yield</th>
<th>Secondary Product</th>
<th>Initial Ash Quality</th>
<th>Cost Range ($/Ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Passivation</td>
<td>1</td>
<td>Same LOI as initial ash</td>
<td>100%</td>
<td>NA</td>
<td>&lt; 6% LOI</td>
<td>$2.00 - $7.00</td>
</tr>
<tr>
<td>Wet Processes</td>
<td>Multiple</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Aerodynamic Classification</td>
<td>2</td>
<td>10% - 40% Reduction in LOI from initial ash</td>
<td>50% - 90%</td>
<td>Variable LOI (typically &gt; 30%)</td>
<td>No Limit</td>
<td>$1.00 - $3.00</td>
</tr>
<tr>
<td>Sieving</td>
<td>2</td>
<td>15% - 50% Reduction in LOI from initial ash</td>
<td>50% - 90%</td>
<td>Variable LOI (typically &gt; 30%)</td>
<td>No Limit</td>
<td>$2.00 - $4.00</td>
</tr>
<tr>
<td>Electrostatic (Belt)</td>
<td>2</td>
<td>1.5% - 3% LOI</td>
<td>60% - 85%</td>
<td>Variable LOI (typically &gt; 30%)</td>
<td>&lt; 20% LOI</td>
<td>$4.00 - $7.00</td>
</tr>
<tr>
<td>Electrostatic (Pneumatic)</td>
<td>2</td>
<td>30% - 60% Reduction in LOI from initial ash</td>
<td>35% - 70%</td>
<td>Variable LOI (typically &gt; 30%)</td>
<td>&lt; 10% LOI</td>
<td>$5.00 - $8.00</td>
</tr>
<tr>
<td>Combustion</td>
<td>1</td>
<td>1.5% - 2.5% LOI</td>
<td>80% - 95%</td>
<td>NA</td>
<td>&gt; 8% LOI</td>
<td>$10.00 - $20.00</td>
</tr>
</tbody>
</table>

Figure 7.4. Relative Cost and Product Quality for Ash Beneficiation Technologies
*NA reflects insufficient data and/or “not applicable”
REFERENCES


APPENDIX – Test Results (Ozone vs. Foam Index)

Test #1 - February 22
PPL Hard Grind Ash, Max Airmerge, 2% O3, O3 Flow = 20 SCFM

Test #2 - February 23
PPL Hard Grind Ash, Min Airmerge, 2% O3, O3 Flow = 13 SCFM
Test #3 - February 24
PPL Hard Grind Ash, Max Fluidized, 2% O3, O3 Flow = 20 SCFM

Foam Index [5 vol-% AEA mL/g-ash]

Dose [lbs of O3/1000 lbs of ash]

Test #4 - February 24
PPL Hard Grind Ash, Min Fluidized, 2% O3, O3 Flow = 8 SCFM

Foam Index [5 vol-% AEA mL/g-ash]

Dose [lbs of O3/1000 lbs of ash]
Test #5 - February 25
PPL Hard Grind Ash, Max Fluidized, 1% O3
O3 Flow = 20 SCFM

Test #6 - March 2nd
PPL Hard Grind Ash, Max Airmerge, 2% O3
O3 Flow = 8 SCFM
Test #7 - March 3rd
PPL Hard Grind Ash, Max Fluidized, 0.5% O3, O3
Flow = 19 SCFM

![Graph showing Foam Index and Dose relationship for Test #7]

Test #8 - March 3rd
PPL Hard Grind Ash, Max Fluidized, 2% O3
O3 Flow = 20 SCFM

![Graph showing Foam Index and Dose relationship for Test #8]
Test #9 - March 11
PPL Regular Grind Ash, Max Fluidized,
2% O3, O3 Flow = 12 SCFM,

Foam index 5 vol-%
AEA [mL/g-ash]

Dose [lbs of O3/1000 lbs of ash]

Test #10 - March 11
PPL Regular Grind Ash, Min Fluidized, 2% O3
O3 Flow = 18 SCFM
Test #11 - March 14
PPL Regular Grind Ash, Max Airmerge, 2% O3
O3 Flow = 12 SCFM

Foam index 5 vol-% AEA [mL/g-ash]

Test #12 - March 15
Dairyland Class C ash, MaxFluidized, 2% O3
O3 Flow = 18 SCFM

Foam Index [mL/g-ash]
Test #13 - March 15
PPL Regular Grind Ash, Max Fluidized, 2% O3
O3 Flow = 18 SCFM

Dose [lbs of O3/1000 lbs of ash] vs. Foam Index 5 vol-% AEA [mL/g-ash]

Test #14 - March 16
Dairyland Class C (Genoa), MaxFluidized, 2% O3,
O3 Flow = 18 SCFM

Dose [lbs of O3/1000 lbs of ash] vs. Foam Index [10 vol-% mL/g-ash]
Test #15 - March 17
Dairyland Class C (Genoa), Max Airmerge
2% O3, O3 Flow = 16 SCFM

Test #16 - March 17
Dairyland Class C (Genoa), MinFluidized
2% O3, O3 Flow = 16 SCFM
Test #17 - March 18
5% AC blended in STI ash, MaxFluidized
2% O3, Flow = 12 SCFM

Dose [lbs of O3/1000 lbs of ash]

Foam Index [25 vol-% mL/g-ash]

Test #18 - March 21
1.5 % AC blended in STI ash, Max Fluidized
2% O3, Flow = 12 SCFM

Dose [lbs of O3/1000 lbs of ash]

Foam Index [10 vol-% AEA mL/g-ash]