2006 MEGA SYMPOSIUM

Paper No. 70

Demonstration of Fly Ash Beneficiaton by Ozonation at PPL Montour SES

R. Afonso, Energy and Environmental Strategies
R. Hurt, I. Kulaots, Brown University
L. LaBuz, PPL
R. Patton, NETL
R. Altman, EPRI

ABSTRACT

The disposal of fly ash from the combustion of coal is becoming increasingly difficult and there is a growing interest in beneficial use alternatives. However, beneficiation is necessary when the fly ash does not meet the required quality specification for the product or market intended.

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, often at a fraction of the of lost sales and/or ash disposal costs. A description of the test system, test results, and preliminary costs for the process are summarized in this paper.

PROJECT 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 SES 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

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)

Because 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

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.

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.

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.

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.

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 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 2 shows that over the same range of ozone input, the unburned carbon is not significantly consumed.

Normalized surfactant adsorptivity

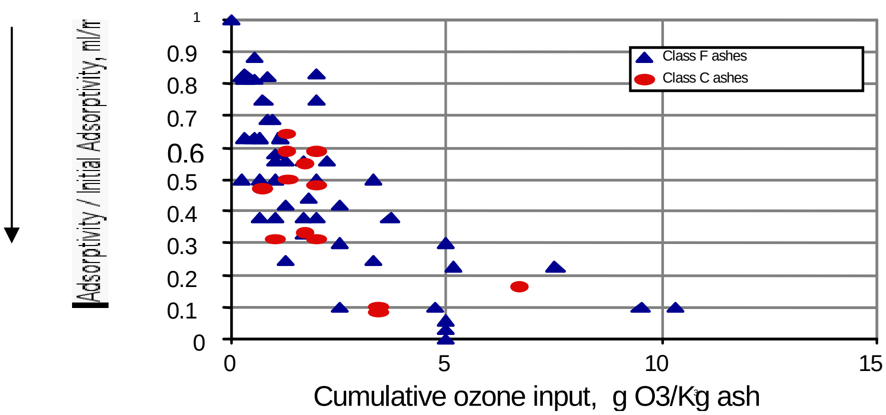

Figure 1. The effect of ozone treatment on surfactant adsorptivity of commercial fly ash samples.

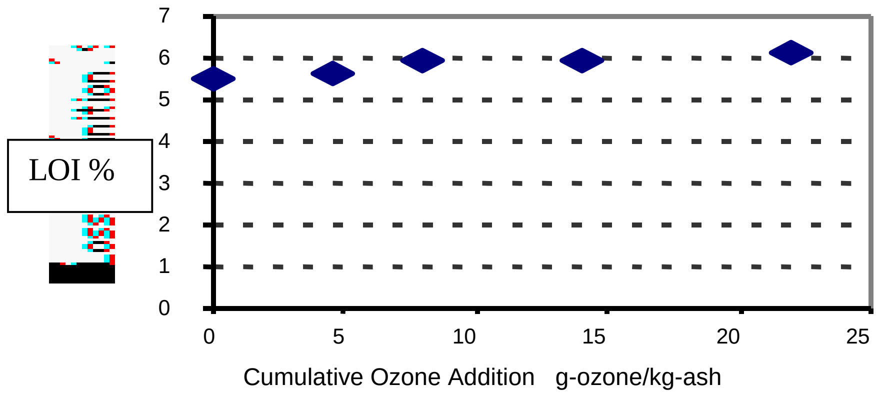

Figure 2. Effect of ozonation on LOI,

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, the side reactions can be minimized and high ozone effectiveness can be achieved.

$$C + O_3 \rightarrow C(O) + O_2 \qquad \text{(chemisorption, desired)} \qquad [1]$$

$$C + O_3 \rightarrow CO / CO_2 \qquad \text{(gasfication, undesired)} \qquad [2]$$

$$O_3 + C(O) \rightarrow 2O_2 + C \qquad \text{(catalytic recombination, undesired)} \qquad [3]$$

Market niche

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 combustion.

MONTOUR SES PROJECT OVERVIEW

The Montour Steam Electric Station (Figure 3), 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. 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).

Figure 3. Montour Steam Electric Station

Figure 4. Montour Station Ash Handling

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 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 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 5 –7.

Figure 5. Ozone generator

Figure 6. Ash ozonation vessel

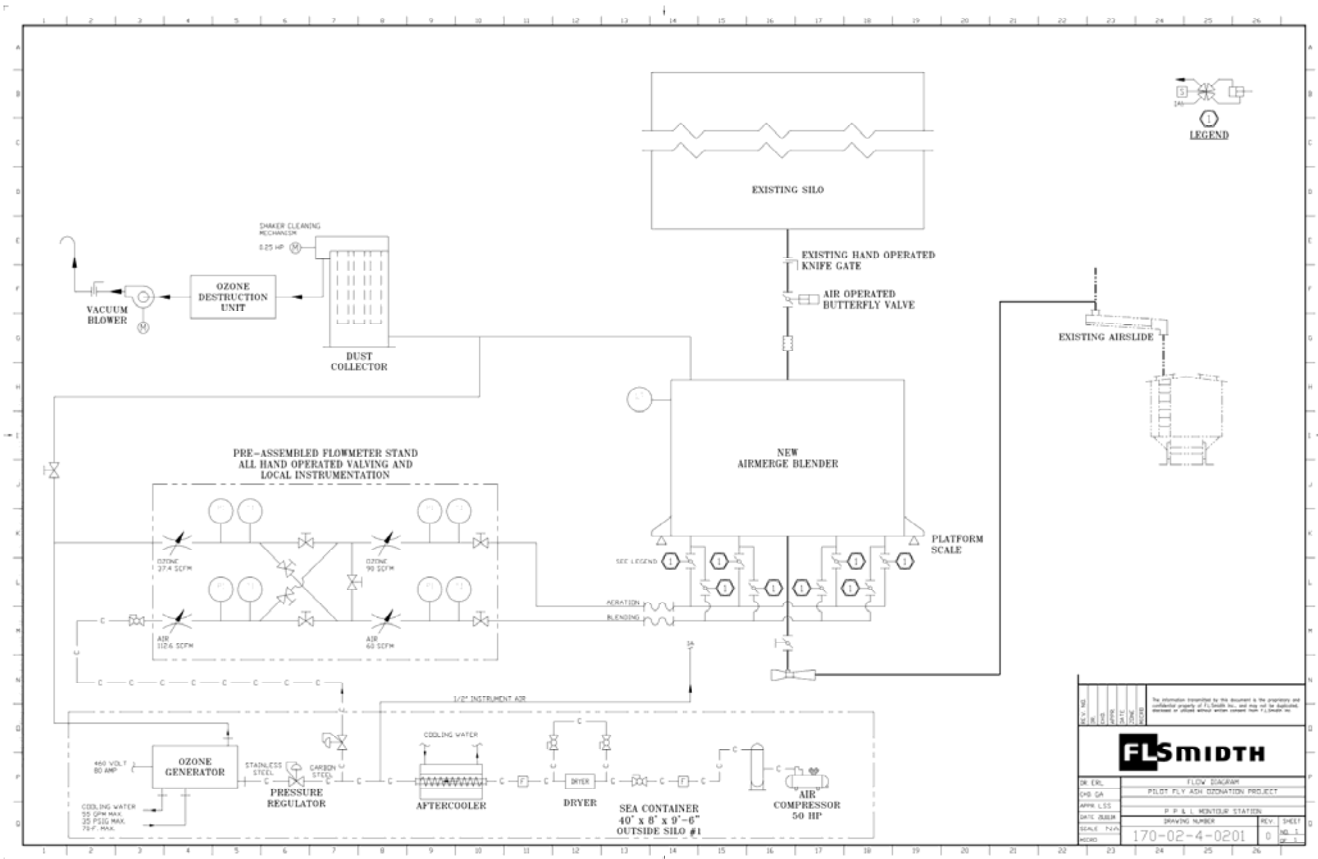

Figure 7. Semi-commercial scale installation of fluidization/ozonation technology at Montour

Test Program – General Approach

A set of parametric tests intended to determine the impacts of the major operating parameters (fluidization, ozone levels, contact times, bed height, velocities) 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 8. It identifies the ash source, type of fluidization approach (Airmerge mode vs. conventional fluid bed mode), as well as other relevant parameters (O_3 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

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.

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.

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%.

Test #	Sample	Test Descriptior	[O3]	O3 Flow	Total Flow
			at generator %	SCFM	SCFM
1	PPL Hard Grind Ash	Max Airmerge	2.0	20	20
2	PPL Hard Grind Ash	Min Airmerge	2.0	13	13
3	PPL Hard Grind Ash	Max Fluidized	2.0	20	20
4	PPL Hard Grind Ash	Min Fluidized	2.0	8	8
5	PPL Hard Grind Ash	Max Fluidized	1.0	20	20
6	PPL Hard Grind Ash	Max Airmerge	2.0	8	20
7	PPL Hard Grind Ash	Max Fluidized	0.5	19	19
8	PPL Hard Grind Ash	Max Fluidized	2.0	20	20
9	PPL Reg Grind Ash	Max Fluidized	2.0	12	35
10	PPL Reg Grind Ash	Min Fluidized	2.0	18	18
11	PPL Reg Grind Ash	Max Airmerge	2.0	12	35
12	Dairyland, Class C	Max Airmerge	2.0	18	70
13	PPL Reg Grind Ash	Max Fluidized	2.0	18	35
14	Dairyland Genoa	Max Fluidized	2.0	16	26
15	Dairyland Genoa	Max Airmerge	2.0	16	26
16	Dairyland Genoa	Min Fluidized	2.0	16	20
17	5% AC & STI Ash	Max Fluidized	2.0	12	12
18	1.5% AC & STI Ash	Max Fluidized	2.0	12	12

Figure 8. 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.

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.

Concrete testing of ozonated and non-ozonated fly ash samples

Concrete test procedure for class F ashes – CMT Laboratories

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.

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.

Concrete test procedure for Class C ashes - American Engineering Testing

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.

RESULTS AND DISCUSSION

Figure 9 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 prviously
- **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)

Test #	Sample	Test Description	LOI	[O3]	[O3]	O3 Flow	Total Flow
			%	at generator %	in bed, %	SCFM	SCFM
1	PPL Hard Grind Ash	Max Airmerge	4.7	2.0	2.0	20	20
2	PPL Hard Grind Ash	Min Airmerge		2.0	2.0	13	13
3	PPL Hard Grind Ash	Max Fluidized		2.0	2.0	20	20
4	PPL Hard Grind Ash	Min Fluidized		2.0	2.0	8	8
5	PPL Hard Grind Ash	Max Fluidized		1.0	1.0	20	20
6	PPL Hard Grind Ash	Max Airmerge		2.0	0.8	8	20
7	PPL Hard Grind Ash	Max Fluidized	2.5	0.5	0.5	19	19
8	PPL Hard Grind Ash	Max Fluidized	3	2.0	2.0	20	20
9	PPL Reg Grind Ash	Max Fluidized	3.2	2.0	0.7	12	35
10	PPL Reg Grind Ash	Min Fluidized		2.0	2.0	18	18
11	PPL Reg Grind Ash	Max Airmerge	4.2	2.0	0.7	12	35
12	Dairyland, Class C	Max Airmerge	0.8	2.0	0.5	18	70
13	PPL Reg Grind Ash	Max Fluidized		2.0	1.0	18	35
14	Dairyland Genoa	Max Fluidized	4.2	2.0	1.2	16	26
15	Dairyland Genoa	Max Airmerge	4.2	2.0	1.2	16	26
16	Dairyland Genoa	Min Fluidized	4.2	2.0	1.6	16	20
17	5% AC & STI Ash	Max Fluidized		2.0	2.0	12	12
18	1.5% AC & STI Ash	Max Fluidized		2.0	2.0	12	12

Figure 9. Test matrix summary

Initial parametric tests

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 10 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.

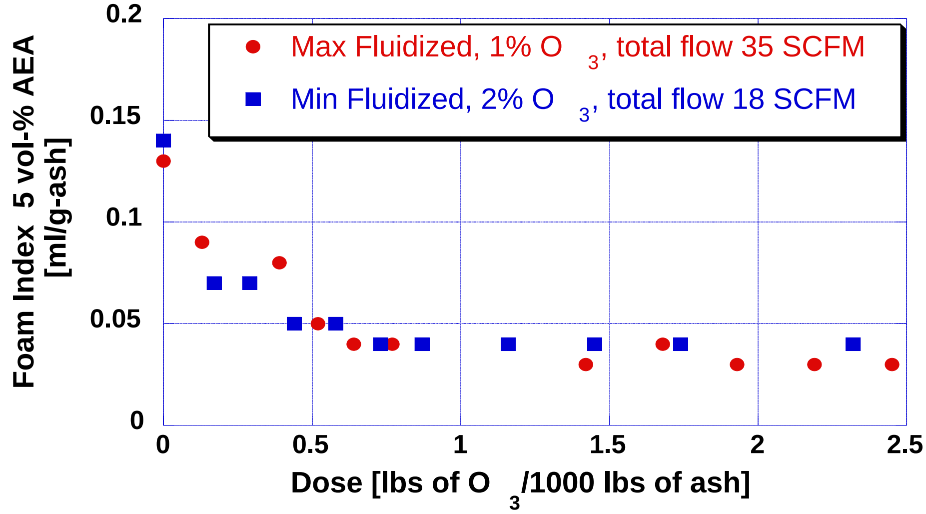

Figure 10. Parametric ozonation tests – effect of fluidization flow rate/velocity

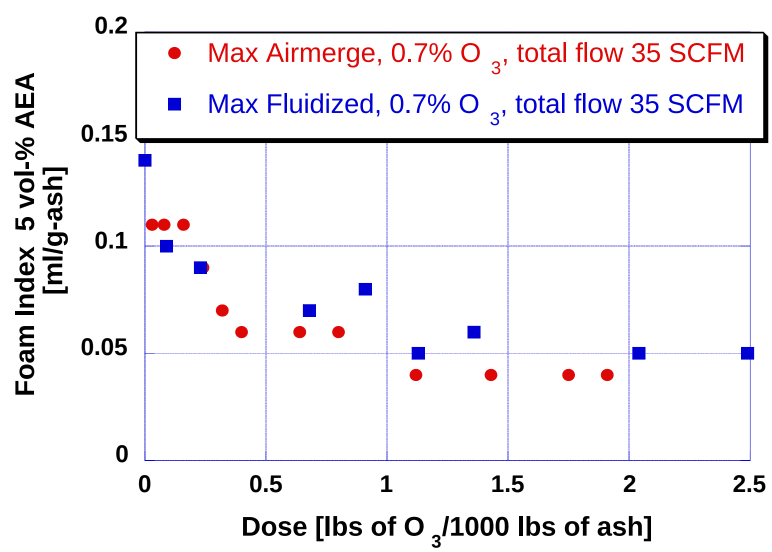

Figure 11. Parametric ozonation tests – effect of different fluidization modes (airmerge vs. simple fluidization)

Figure 11 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 12 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.

Test #	Sample	LOI	Foam Index	Foam Index	% AEA Untreated ash	% Air	Air Loss rate
			Untreated Ash	Ozonated Ash [end test]	divided by	at end of test	
		%	5 vol-% AEA ml/g-ash	5 vol-% AEA ml/g-ash	%AEA Portland Cement	%	% per 90 min
1	PPL Hard Grind Ash	5.2	0.16	0.04	600		
2	PPL Hard Grind Ash		0.07	0.04			
3	PPL Hard Grind Ash		0.1	0.02		4	4.2
4	PPL Hard Grind Ash		0.11	0.01			
5	PPL Hard Grind Ash		0.11	0			
6	PPL Hard Grind Ash		0.09	0.01	240		
7	PPL Hard Grind Ash	2.5	0.09	0.03	240	4.6	3
8	PPL Hard Grind Ash	3	0.1	0.03	280	4.1	2.9
9	PPL Reg Grind Ash	3.2	0.14	0.05	240	3.9	4.1
10	PPL Reg Grind Ash		0.14	0.04		4.4	2.2
11	PPL Reg Grind Ash	4.2	0.14	0.04	500	3.1	3.1
12	Dairyland, Class C	0.8	0.08	0.02		6.7	1.3
13	PPL Reg Grind Ash		0.13	0.03		4.8	3.7
14	Dairyland Genoa	4.2	0.24	0.06		5.1	1.1
15	Dairyland Genoa	4.2	0.2	0.02			
16	Dairyland Genoa	4.2	0.18	0.02		3.7	1.8
17	5% AC & STI Ash		0.9	0.65			
18	1.5% AC & STI Ash		0.36	0.04	600	3.5	3.3
	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				6.7	1.3

Figure 12. 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 13). 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)

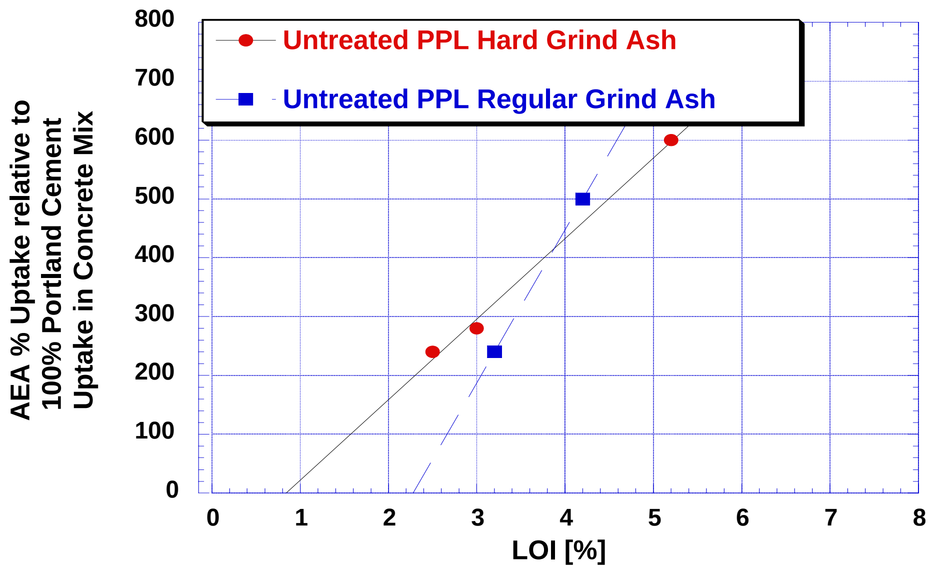

Figure 13. %AEA versus LOI for two PPL Class F ashes.

- 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

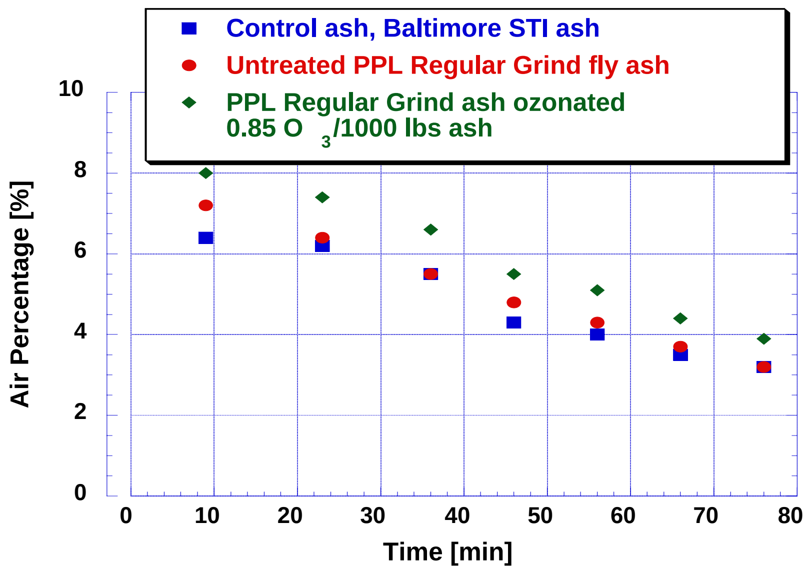

Figure 14. PPL regular grind ash concrete test results – test #9

Figures 14 and 15 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 Figure15, which has an air entrainment very similar to the reference ash. Further, it should be noted that the untreated ash in Figure 14 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.

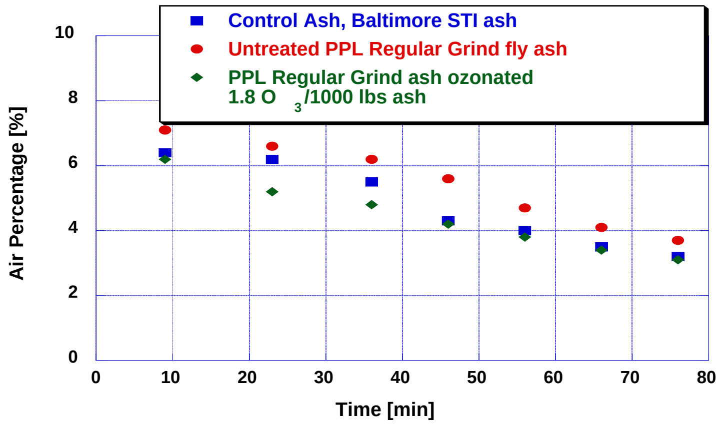

Figure 15. PPL regular grind ash concrete test results – test #11

PPL Hard Grind Ash

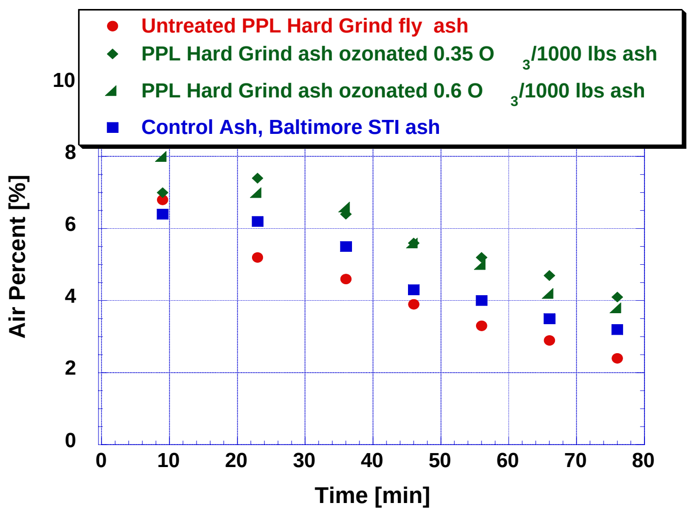

Figure 16. PPL hard grind ash concrete test results – test #8

Figure 16 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%

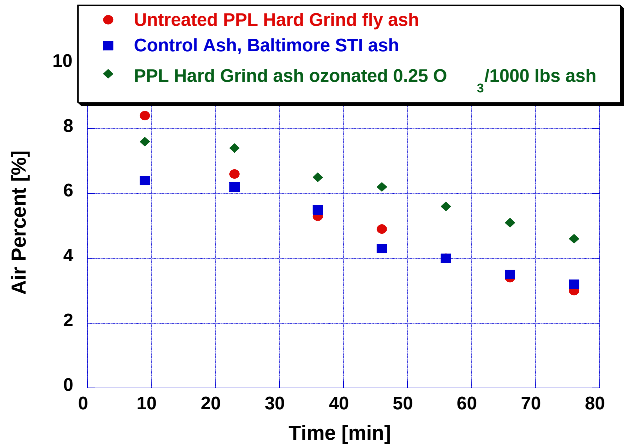

Figure 17. PPL hard grind ash concrete test results – test #7

Figure 17 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 16. 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

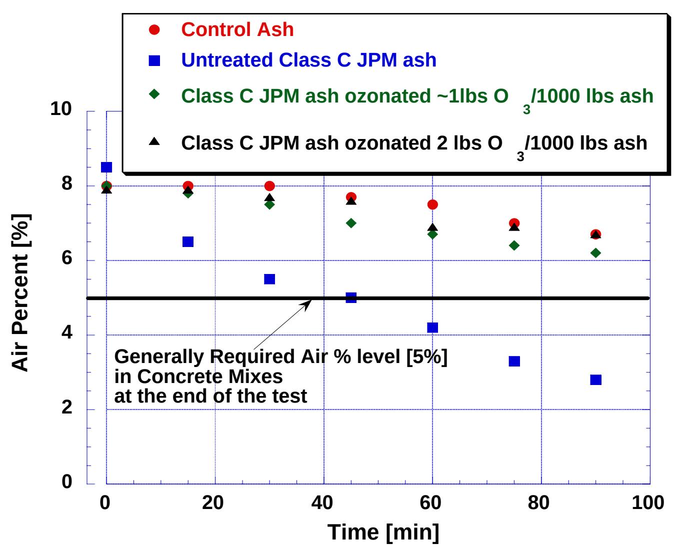

Figure 18. Dairyland JPM class C ash concrete test results – test #12

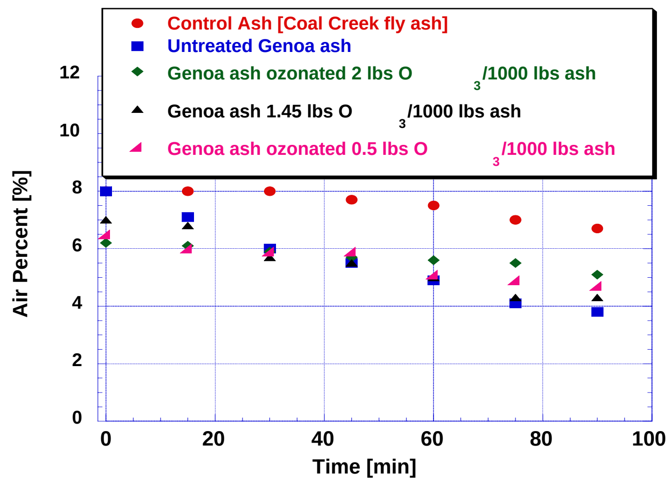

Figure 19. Dairyland Genoa Class C/F blend ash concrete test results – test #14

Figures 18 and 19 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 20 below

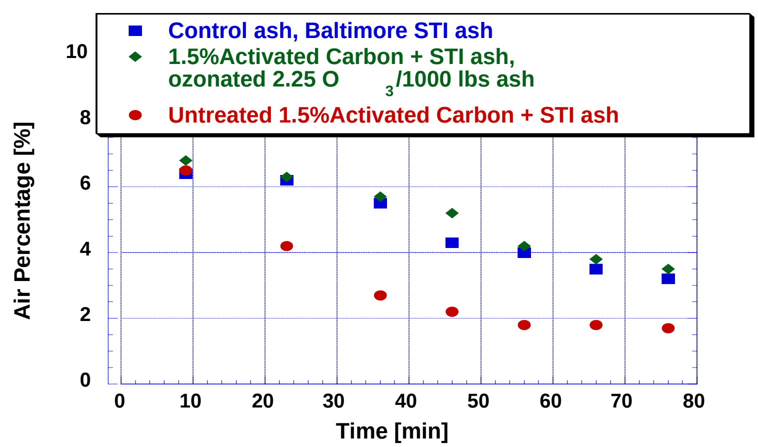

Figure 20. Class F (STI Baltimore) mixed with 1.5% Activated Carbon concrete test results – test#18

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 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 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.

Budgetary Cost Estimate

A brief cost analyses was conducted 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.

The scale up criteria was predicated on Montour SES ash management considerations. The resulting technology design package was 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)

Capital Cost

A budgetary estimate was developed for the Montour SES. Budgetary capital costs are summarized in Figure 21.

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

Figure 22 summarizes the energy requirements for the technology

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

Equipment and Budgetary Costs	Cost, $k
Equipment and Services	
Engineering	400
Ozone Generation and Destruction	1,800
Ash Filling, Blending, Filtration	450
Ash Conveying	200
Bin and Load Out	275
Total	3,125
PPL Equipment	275
Ash Conveyor Piping and Fittings	
Air Compressor Piping, Ductwork, Hand Valves	
Ozone System Piping and Hand Valves	
Water Drain Piping	
Ozone Generation Building (OGB)	
Heating System for OGB	
Pipe Hangers and Stanchions	
Structural Steel Tower for Blenders and Load Out	
PPL Installation Services	775
Install Ozone Generation System	
Other Mechanical Installation	
Electrical and Controls Installation	
PPL Total	1,050
Shipping	80
Contingency (10%)	425
Total Estimated Equipment Cost	4,680

Figure 21. Budgetary Capital Cost Estimate

ELECTRICAL LOAD LIST Fly Ash Ozonation - 220 ton / 8 hr shift										
LOAD DESCRIPTION		LOAD TYPE		THREE-PHASE LOADS			MOTORS			
EQUIPMENT/SYSTEM	SUBSYSTEM	C	I	H.P.	KW	V	S.F.	NOMINAL RPM	ENCLOSURE TYPE
AT EXISTING SILO #2									
Ash Conveying	FK Pump A		I	50		480	1.15	1200	TEFC
Ash Conveying	PD Blower Package		I	150		480	1.15	1800	TEFC
AT BLEND / LOADOUT									
Ash Conveying	FK Pump B		I	50		480	1.15	1200	TEFC
Ash Loadout	Dry Spout		I	0.5		480	1.15	1800	TEFC
Dust Collection	Loadout Vent Filter Fan	C		5		480	1.15	3600	TEFC
AT OZONE BUILDING									
Ozone Generation	Compressor A	C		150		480	1.15	1800	TEFC
Ozone Generation	Compressor B	C		150		480	1.15	1800	TEFC
Ozone Generation	Refrigerant Dryer A	C			6.3	480	--	--	--
Ozone Generation	Refrigerant Dryer B	C			6.3	480	--	--	--
Ozone Generation	Ozone Generator A	C			200	480	--	--	--
Ozone Generation	Ozone Generator B	C			200	480	--	--	--
Ozone Generation	Ozone Destruct A	C			21	480	--	--	--
Ozone Generation	Ozone Destruct B	C			21	480	--	--	--
Ozone Generation	Clean Fan A	C		20		480	1.15	3600	ODP
Ozone Generation	Clean Fan B	C		20		480	1.15	3600	ODP
Ozone Generation	Cooling Water Pump (estimate)	C		10		48	1.15	1800	TEFC
480 VAC TOTALS				**606**	**455**	**480**			

Figure 22. System energy consumption summary

Using the parameters above yields the results summarized in Figure 23

ASH PROCESSED RANGE (TPY)	ENERGY COST ($/YR)	CAPITAL COST RANGE ($/YR)	LABOR COST ($/YR)	TOTAL COST RANGE ($/YR)	TOTAL COST RANGE ($/TON)
135K – 205K	**225K – 340K**	**468K**	**100K**	**703K – 908K**	**4.5 – 5.2**

Figure 23. Summary of Ozonation Technology Costs

The range of $4.5 - $5/ton seems compatible with previous preliminary assessments. (for example see "*Beneficiation of Fly Ash Containing Mercury and Carbon*", EPRI, Palo Alto, CA: 2005. 1004267).

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.

REFERENCES

“Beneficiation of Fly Ash Containing Mercury and Carbon”, EPRI, Palo Alto, CA: 2005. 1004267.

“Novel Ash Beneficiation Processes for Managing Unburned Carbon and Ammonia”, EPRI, Palo Alto, CA: 2002. 1004395.

“Ozonation for the Chemical Modification of Carbon Surfaces in Fly Ash," Gao, Y., Külaots, I., Chen, X., Aggarwal, R., Mehta, A., Suuberg, E.M., Hurt, R.H., *Fuel* 80 765-768 (2001).

"The Role of Carbon Surface Chemistry in Fly Ash Utilization and the Potential for Ash Beneficiation by Ozone," Hurt, R.H., *Energeia*, 13 4 2002.

"Mechanisms of Surfactant Adsorption on Nonpolar, Air-Oxidized, and Ozone-Treated Carbon Surfaces," Chen, X., Farber, M., Gao, Y., Kulaots, I., Suuberg, E.M., Hurt, R.H., *Carbon* 41 (8) 1489-1500 (2003).

"Interactions of Carbon-Containing Fly Ash with Commercial Air Entraining Agents for Concrete," Freeman, E., Gao, Y.M., Hurt, R.H., Suuberg, E.S. *Fuel*, 76 (8) 761-765 (1997).

"Effects of Carbon on Air-Entrainment in Fly Ash Concrete: The Role of Soot and Carbon Black," Gao, Y.; Shim, H.; Hurt, R.H.; Suuberg, E.M.; Yang, N.Y.C. *Energy and Fuels*, 11, 457-462 (1997).

"Surfactant Adsorptivity of Carbon Solids from Pulverized Coal Combustion under Controlled Conditions", Hachman, L., Burnett, A., Gao, Y., Hurt, R., Suuberg, E. *Twenty-Seventh Symposium (International) on Combustion*, 2965-2971, The Combustion Institute, Pittsburgh, 1998.

"Adsorptive and Optical Properties of Fly Ash from Coal and Petroleum Coke Cofiring," Yu, J., Külaots, I., Sabanegh, N., Gao, Y., Hurt, R.H., Suuberg, E.S., Mehta, A. *Energy and Fuels*, 14 (3) 591-596 (2000).

"The Effect of Solid Fuel Type and Combustion Conditions on Residual Carbon Properties and Fly Ash Quality," Gao,, Y., Kulaots, I., Chen, X., Suuberg, E.M., Hurt, R.H. *Proc. Comb. Institute*, Vol. 29 475-483 (2002).

"Dry and Semi-Dry Methods for Removal of Ammonia from Fly Ash," Gao, Y., Chen, X., Fujisaki, G., Mehta, A., Suuberg, E.M., Hurt, R.H., *Energy and Fuels*, 16 1398-1404 (2002).

"Alternative Beneficiation When Conventional Approaches Can Not Be Justified". Afonso, R., et al.; Pittsburgh, PA. NETL Conference on Unburned Carbon on Utility Fly ash. (May 2000).

"Customizing Fly ash Beneficiation for Physical Characteristics and Market Drivers". Afonso, R., et al. Atlanta, GA. EPRI/DOE/EPA Mega Symposium. (August 1999).