CLEANABILITY OF ENRICHED FLY ASH CARBONS FOR THEIR UTILIZATION AS FEEDSTOCKS FOR CARBON MATERIALS

ANNUAL TECHNICAL PROGRESS REPORT **

Reporting Period Start Date: *January 1, 2001*

Reporting Period End Date: *April 15, 2002*

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DOE Award number: DE-FC26-98FT40350

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*** This project has a no-cost extension till May 31, 2002. An addendum to the present report summarizing the work conducted during the remaining period will be submitted after the project ending date.*

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Abstract

The implementation of increasingly stringent Clean Air Act regulations by the coal utility industry has generally resulted in high carbon fly ashes, that are rendered unsuitable as additives for the cement industry, and consequently, they are disposed. It is estimated that in 1998 around 6 million tons of unburned carbon were disposed due to the present lack of efficient routes for its utilization. Accordingly, Phase 1 and 2 of this research program conducted extensive studies on the characterization of unburned carbon and established routes for its utilization for the production of activated carbons and carbon artifacts. However, the unburned carbon must meet certain ash purity requirement for its utilization as precursor for carbon materials. Therefore, the overall objective of Phase 3 of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for carbon materials.

Following the previous industrial test in Phase 2 at Shawville power station (Reliant Energy), which successfully complied with DEP environmental requirements and it was shown that the carbon can be successfully concentrated in selected hoppers, the fly ash carbons have been further beneficiated by various conventional commercial techniques in the present report. The one-step activation process to utilize unburned carbon from coal combustion by-products to generate activated carbons has also been further investigated and optimized. The pretreatment protocol has been proposed and demonstrated to promote the microporous structure of resultant activated carbon.

The work reported in this report has also demonstrated the feasibility of application of froth flotation for the separation of power plant fly ash into carbon and ash streams, while the chemical digestion applied resulted in a fly ash sample with an ash content ~37wt%, and a fly ash carbon stream with ash content ~1wt%. By pretreating the fly ash carbons with 1.5wt% KOH, the surface area of the resultant activated carbon increased 35.5%, while retaining relatively high solid yields. For the second pretreatment method investigated here, the surface area of resultant activated carbon increased ~11-60%. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hours, where the resultant activated carbon has a surface area of 854m^2/g and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

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1. Introduction

1.1 Rationale

The coal industry provides nowadays the main energy source for electricity generation in the US, where in 1999 the combustion of over 930 million tons of coal (around 90% of the total coal production) was used in coal-fired units to generate over 55% of the total electricity[1]. However, this also generated over 60 million tons of fly ash and around 6 million tons of unburned carbon [2]. Nowadays, the fate of these byproducts is mainly disposal due to the lack of routes for their utilization. Furthermore, the implementation of increasingly stringent Clean Air Act Regulations by the coal utility industry has resulted in an increase in the concentration of unburned carbon in coal combustion fly ash. This has restricted the principal use of ash in the cement industry, since the unburned carbon tends to adsorb air-entrainment agents that are added to the cement to prevent crack formation and propagation [2]. Consequently, the coal utility industry is facing potential annual losses of $400 millions from the ash revenue and $200 million from increasing disposal costs. The alternatives for the utility industry are to begin offsetting coal combustion with natural gas, or require additional coal cleaning to remove the ash prior to combustion, or simply start utilizing the unburned carbon. The first two alternatives would clearly jeopardize the future of the coal industry in this country. Accordingly, during Phase I and II of this research program, the authors conducted extensive studies on the characterization of unburned carbon, also referred to as fly ash carbon, from different coal-fired power plants and assessed its potential for the generation of premium carbon products[2,3]. Two potential routes were identified: (i) the use of unburned carbon as precursor for the production of activated carbons[4]; and (ii) the utilization of unburned carbon as a substitute for calcined petroleum coke in the production of carbon bodies[5]. The work conducted demonstrated the ability of unburned carbon from coal-fired power plants to generate activated carbons by one simple step activation process, in contrast to conventional precursors that require a two-step process (devolatilization and activation). Furthermore, after only 60 minutes activation time, the unburned carbon samples generated activated carbons with

microporous structure and surface areas close to 500 m^2/g [3]. For the case of the carbon bodies, the unburned carbon samples present similar thermal history to that of calcined petroleum coke and the density of the carbon pellets prepared with unburned carbon was comparable to that using only petroleum coke [3]. Therefore, Phases I and II of this research program indicated that the added value generated from the unburned carbon utilization would bring substantial additional revenues to the coal-fired plants, where a ton of activated carbon sells for around $400-$5,000 and calcined petroleum coke usually costs around $200/ton. However, the unburned carbon must meet the ash purity requirement for its utilization as precursor for carbon materials. For instance, to serve as a precursor in the production of activated materials, fly ash carbons must compete against wood precursors, that present very low ash contents (<5%). The ash requirement becomes even more stringent for the case of carbon artifacts, where typical commercial cokes contain less than 0.5% ash. Clearly, this cleanability issue stands in the way for the coal utilities to start commercializing the unburned carbon as a feedstock for carbon materials.

1.2 Potential markets for unburned carbon

The utilization of unburned carbon can bring enormous ecomomical and environmental benefits to both the coal and utility industry. Although several technologies have been successfully developed to separate the unburned carbon from the fly ash, only a few power plants have installed a beneficiation process on their sites. This is due to the low value of the resultant separated materials, since a ton of fly ash generally sold for as little as $10-20, and the unburned carbon is simply disposed or rerouted to the combustor. However, the economics of this process can be greatly enhanced if both separated materials can be used as precursors for high-value products. In fact, this is the case for the unburned carbon, which can be used as an excellent precursor for the generation of premium carbon products, like activated carbons and carbon artifacts. Therefore, the added value generated from the unburned carbon utilization would clearly offset the cost of the separation process. For instance, the average price for a ton of activated carbon ranges from $500 up to $4000, which implies a potential 25-200 fold

increase compared to the price of the ash (<$20/ton). For the case of carbon artifacts, the calcined petroleum coke used for their manufacture usually costs ~$220-250/ton.

1.2.1. Activated carbons

The present global consumption of activated carbons is over 350,000 tons and it is estimated to rise around 7% annually. The main reason for this expanding market is the ubiquitous use of activated carbons as adsorbent materials in a broad range of increasing household, medical, industrial, military and scientific applications. These range from gas-phase adsorption in household air conditioning equipment and industrial emissions control, to liquid-phase adsorption for water treatment and even gold recovery. Due to the expanding market for activated carbons, especially in applications related to environmental protection, new precursors are being sought. However, for these new precursors to compete effectively with conventional raw materials, such as wood, they must be inexpensive, have a low mineral matter content and be easily converted into activated carbons. The unburned carbon in the fly ash furnishes satisfactorily all these conditions, since it can (1) be easily obtained from the utility industries as a by-product; (2) beneficiated from the fly ash by commercially available techniques; and (3) it has already gone through a devolatilization process while in the combustor and, therefore, only requires to be activated [6,7].

1.2.2 Carbon artifacts: petroleum coke substitute

Currently, 6 million tons of calcined petroleum coke, worth around $1,200 million, are sold annually in US for the manufacture of carbon artifacts. Even though calcined petroleum coke is the dominant precursor for carbon artifacts, the unburned carbon from coal combustion is a potential competitor, as described here. The unburned carbon has been treated at temperatures well above 1200-1300°C, and can be regarded as calcined coke. For instance, the H/C atomic ratios of the unburned carbon are below 0.02 and they are comparable with commercial precursors for carbon artifact production, where the typical H/C atomic ratios are around 0.01 [8]. The challenging issue in this task will be to meet the purity requirement, since typical commercial cokes contain less than 1% ash, preferably in the 100-300 ppm range. Sink/float methods using a high-density

liquid media can effectively enrich the carbon content, by reducing the ash to around 10-20% [9]. Other methods, such as acid digestions, can further reduce this value. Previous work conducted on the removal of mineral matter from coal, has shown that ash levels as low as 100-200 ppm are readily achieved by acid digestion [10]. Therefore, the unburned carbon from coal combustion could be a strong competitor to petroleum coke for the production of carbon artifacts.

1.3. Program objectives and research design

The overall objective of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for activated carbons. Due to financial constraints, it was not possible to investigate further in great depth the utilization of fly ash carbons for carbon artifact production.

1.3.1. Task 1: Suite procurement and characterization

A suite of coal-fired power plant fly ash were procured and characterized at The Pennsylvania State University. The samples were selected from the different hoppers located in Units #1 in a coal-fired power plant operated by Reliant Energy and located at Shawville, PA. During Phase 1 of this project, a detailed study of a series of fly ash hoppers of Unit #4 of the same plant revealed the presence of fly ash carbons with an ash content <50% [2], and during Phase 2 of this project, an industrial test was conducted on Unit #4 to implement the Carbon Plus separation technology to precipitate selectively the unburned carbon [3]. Additionally, samples from The Pennsylvania State University research boiler was also included in the suite. The samples were characterized using a battery of tests, previously developed by the authors and that includes thermogravimetric profiles, proximate analyses and elemental analysis, as well as petrographic analyses. Furthermore, the properties of these high-carbon fly ash samples towards their use as precursors for carbon products were also investigated. This evaluation included the study of their inherent properties, such as porous structure.

1.3.2 Task 2: Cleanability of fly ash carbons

As previously described, the challenging issue in the utilization of carbon from fly ash is to meet the ash purity requirement of precursors for carbon materials. Accordingly, this task was divided into the following subtasks: (2a) froth flotation, (2b) float/sink, and (2c) chemical digestions.

1.3.2.1. Task 2a. Froth flotation Bench scale froth flotation tests were conducted in The Penn State University on the above samples.

1.3.2.1. Task 2b. Float/sink Bench scale float/sink tests are presently being conducted at The Penn State University on the above samples and the results will be reported later on the addendum to the current annual report.

1.3.2.3 Task 2c. Chemical cleaning Preliminary studies conducted during Phase 1 and Phase 2 of this project have shown that ash levels can be reduced to <0.5% by standard acid digestion methods, and this protocol was further explored and optimized during Phase 3 at The Pennsylvania State University [10]. The ultimate goal of this Task is to facilitate a process, that can reduce the inorganic content of fly ash carbon to levels acceptable for the manufacture of carbon products, while still being an economically sustainable beneficiation process.

1.3.3. Task 3: Production of premium carbon products

The high purity carbon samples obtained from the above enrichment process were used to produce premium carbon products at the Pennsylvania State University following the protocols successfully developed in Phase 1 and 2 of this project. The activation of the fly ash carbon was carried out in a vertical tube furnace [2]. During Phase 1 and 2, the authors demonstrated that a one-step process, that includes simultaneous carbonization and activation, can be employed successfully for these materials. This is due to the thermal history of the fly ash carbon, that has already gone through a devolatiliztion step while in the combustor, and therefore, only requires to be activated. The activation process was further optimized. Furthermore, during Phase 3 the pretreatment process was

proposed and investigated to promote the porosity of the activated carbon from fly ash carbon. The properties of the activated carbons were systematically characterized at The Pennsylvania State University, including a detailed description of the porous structure (micropores or <2nm in width, mesopores or 2-50nm in width, and macropores or >50nm in width [11]) using conventional adsorption techniques, like N_2 adsorption isotherms at 77K.

In addition, the characterization of fly ash carbon also allowed to compare its properties with those of commercial carbon precursors for carbon artifacts, according to their H/C atomic ratio, petrographic evaluation and porosity analysis [5].

2. EXECUTIVE SUMMARY

The implementation of increasingly stringent Clean Air Act regulations by the coal utility industry has generally resulted in high carbon fly ashes, that are rendered unsuitable as additive for the cement industry, and consequently, they are disposed. It is estimated that in 1998 around 6 million tons of unburned carbon were disposed due to the present lack of efficient routes for its utilization. Accordingly, Phase 1 and 2 of this research program conducted extensive studies on the characterization of unburned carbon and established routes for its utilization for the production of activated carbons and carbon artifacts. However, the unburned carbon must meet certain ash purity requirement for its utilization as precursor for carbon materials. Accordingly, the overall objective of Phase 3 of this research program is to evaluate the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for carbon materials.

This research program firstly included the selection and characterization of a suite of coal-fired power plant fly ashes. The sample procurement was carried out by Reliant Energy and The Pennsylvania State University. The characterization of this suite included thermogravimetric profiles, particle size distribution, and proximate analyses. An industrial test conducted during Phase 2 at Shawville power station, that uses 1,500 tons of coal per day and is operated by Reliant Energy, showed that that the carbon can be successfully concentrated in selected hoppers, while successfully complying with DEP environmental requirements. Following the previous industrial test, the fly ash carbons have been further beneficiated during Phase 3 by various conventional commercial techniques, and the results are reported here. In addition, following the previous work in Phases 1 and 2 that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the one-step activation process was further investigated and a pretreatment protocol was proposed and optimized to generate activated carbons with properties similar to conventional commercial activated carbons.

The work reported in this report has demonstrated the feasibility of the application of froth flotation for the separation of power plant fly ash into carbon and ash stream. From a fly ash sample collected from Shawville station with a carbon content or LOI (loss-on-ignition) of 17%, it was possible to obtain a carbon stream with LOI of 70% and ash stream with LOI of 2.5% by applying froth flotation. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Chemical digestion has also been applied to a fly ash sample with an ash content of ~37wt%, and the resultant fly ash carbon stream has an ash content of only ~1wt%.

Following the previous work that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the work reported here has also further investigated and optimized two kinds of pretreatment process to promote the microporous structure of the resultant activated carbon. After 2 hours steam activation, activated carbons with surface area up to 540m^2/g have been generated from the unburned carbon in combustion waste. Pretreatment of the unburned

carbon with 1.5wt% KOH, resulted in a 35.5% increase of the surface area of the resultant activated carbon, while retaining relatively high solid yields. For the second pretreatment method, all the different pretreatment conditions studied in the report promote the porosity of resultant activated carbons, where the surface area increases ~11-60%. With increasing pretreatment time, there is an increase in the porosity (surface area and pore volume) of the resulting activated carbons. However, for extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores, and an increase of the total pore volumes. Furthermore, with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hr, where the resultant activated carbon has a surface area of $854m^2/g$ and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

In addition, the work reported here also included the characterization of fly ash carbons. The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows a very high carbon content (97.7%), and conversely, low hydrogen content (0.02%), that are comparable with values also reported for conventional calcined petroleum coke. Furthermore, the sulfur content of the unburned carbon is significantly lower than that of petroleum coke, 0.94% vs. 3.42%. In contrast, the density of unburned carbon is somewhat lower than for petroleum coke, probably due to its surface area, that is created by the rapid heat treatment experienced in the combustor by the unburned carbon. Furthermore, both the unburned carbon and the petroleum coke present isotropic and anisotropic textures, where a given ratio of anisotropic over isotropic coke is required for different applications.

Finally, the long-term benefits of this research program can be summarized as follows: (i) the coal industry will continue being the main provider to the utility industry, where currently around 1 billion tons of coal are sold annually; (ii) the carbon industries, such as those producing activated carbons, will have cost-effective and novel precursors; and (iii) this program prevents pollution at its source by simultaneously reducing NOx emissions and byproduct waste streams, including unburned carbon and ash, and will therefore have a vast benign environmental impact.

3. EXPERIMENTAL

3.1 Procurement and characterization of fly ash carbon samples

Reliant Energy conducted the procurement of the fly ash samples in the Shawville station Unit #1 and #2 (Bradford Township, PA). This unit has been retrofitted with a low-NOx burner, and uses primarily Lower, Middle and Upper Kittanning and Lower and Upper Freeport seam coal. The sampling procedure was conducted all along the electrostatic precipitator of each train. The procedure used was to put the systems on hand and "pull" on each hopper in turn until plant personnel was sure that the hoppers were empty. Once all the hoppers on that boiler were certified as empty, they then went back, shut down the ash transport system and then got a hand sample (5 gallons) from each hopper in turn, thus assuring that the ash in the sample was "fresh ash" [3].

Additionally, another sample was also procured from PSU research boiler, which has been also retrofitted with a low-NO_x burner and uses a high volatile bituminous coal from Middle Kittanning seam.

The loss-on-ignition (LOI) contents of the fly ashes assembled were determined according to the ASTM 311 procedure. There analyses were conducted in duplicates. For fly ashes commonly derived from Eastern U.S. coals, the LOI value essentially equates to carbon content. The elemental analysis were conducted using a Leco CHN-600 analyzer. The petrographic analyses were performed on epoxy-bound polished pellets under polarized reflected white-light at 625X magnification and oil-immersion using a Zeiss Universal Research microscope. The thermogravimetric analysis were conducted on a Perkin Elmer TGA7. The porosity of the samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT [5].

3.2. Beneficiation of fly ash carbons

In order to determine the feasibility of pursuing the use of froth flotation for separating fly ash into two utilizable products: low ash carbon and low carbon ash, a fly ash sample with a carbon content of 16.3% from the coal-fired power plant at Shawville, PA, which is operated by the CPCPC member Reliant Energy, was used for the froth flotation study. A conventional laboratory froth flotation cell and conventional coal froth flotation reagents were applied to the test. An initial flotation test was conducted to determine the approximate reagent level to obtain carbon recovery and a stable froth. Based on its results, the second test with circuit variation was conducted, including a scavenger stage to remove additional carbon from the ash product and various cleaning stages to reduce the ash content in the carbon product [12]. Other froth flotation separation test were conducted on the fly ash sample with a carbon content of 58.3% from the Penn State University research boiler.

An acid digestion step was also conducted by following conventional HCl/HF treatments [13] under both room temperature and also at 65°C to further reduce the ash concentrations [14]. The enriched fly ash carbon was then dried and subsequently characterized by conducting LOI measurements and 77K N_2 adsorption isotherms.

3.3. Production of activated carbon

The unburned carbon samples (A) was firstly pretreated at 400°C for 2 or 3 hours, and the unburned carbon sample (B) was impregnated with potassium hydroxide (KOH) and dried at 110°C for 6 hours (B-KOH). Then the activation of the samples was carried out in an activation furnace that consists of a stainless steel tube reactor inside a vertical tube furnace. The sample with or without pretreatment was held isothermally at 850°C for 1-3 hours in flowing steam [15]. The porosity of the samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The total pore volume, V_t was calculated from the amount of vapor adsorbed at the relative pressure of 0.95, and the total surface area S_t was calculated by standard BET equation.

4. RESULTS AND DISCUSSION

4.1. Procurement and characterization

A total of 14 fly ash samples containing unburned carbon were collected from Shawville station unit #1 (Bradford Township, PA), that is operated by Reliant Energy. This unit has been retrofitted with a low-NOx burner, and uses primarily Lower, Middle and Upper Kittanning and Lower and Upper Freeport seam coals. Samples were collected from the Research-Cottrell Precipitator hoppers #1-8 and Buell precipitator hoppers #9-14. Following the gas flow direction, the hoppers #1-4 are located in the first row and the hot-side, while hoppers #5-8 are in the second row and hoppers #9-14 are in the third row. During Phase 1 and 2 of this project, samples from Unit #4 were collected and characterized. Figure 1 shows the LOI of all fly ash samples and the hopper configuration and gas flow direction are also indicated.

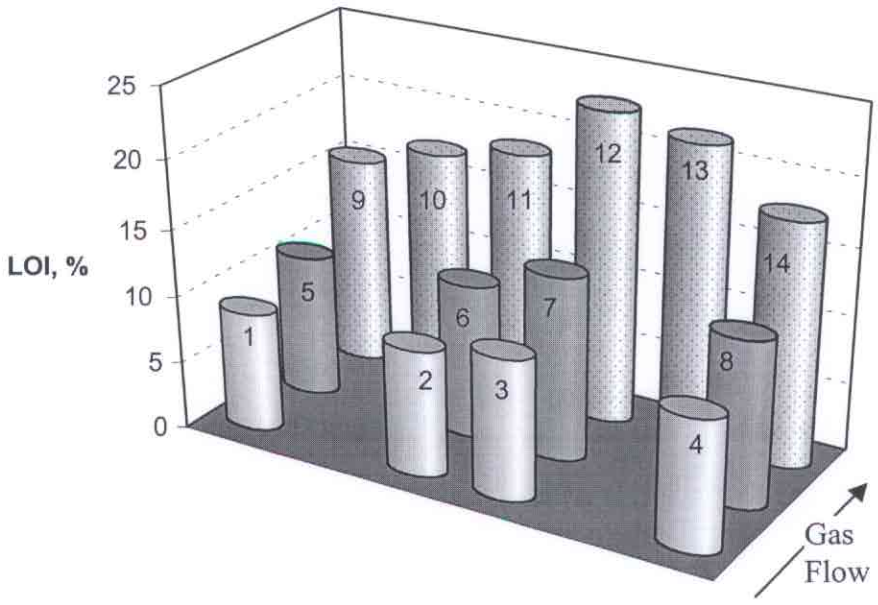

Figure 1. Variation in LOI of the fly ashes collected from Shawville Unit #1, where the gas flow direction is indicated.

The loss-on-ignition (LOI) of all the 14 fly ash samples was determined according to the ASTM C 311 procedure, as described during Phase 1, and all the analyses were conducted in duplicates. As shown in Phase 1, the fly ash samples collected from the hot-side hoppers (#1-4) present the lowest LOI contents of only 8.8-9.7% (Figure 1). The LOI values become higher for hoppers in cool-side, where the LOI for the second row of hoppers #5-8 are 10.6-13.6%, while the third row hoppers #9-14 have the highest LOI of 15.7-22.9%.

4.2. Cleanability of fly ash carbons

4.2.1. Froth flotation

An initial flotation test was conducted to determine the approximate reagent level to obtain carbon recovery and a stable froth. Based on its results, the second test with circuit variation was conducted, including a scavenger stage to remove additional carbon from the ash product and various cleaning stages to reduce the ash content in the carbon product. The separation results including the LOI and yield for each fraction is shown in Figures 2 and 3. The result from the circuit variation test indicates that it is feasible to produce a low carbon ash product (< 3% LOI) using froth flotation. According to this test work, a second stage of flotation to remove additional carbon from the ash is required. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Additional test work will evaluate the use of higher concentrations of reagents to achieve this in one stage of flotation. The yield of low carbon ash was 62% in this test work with this sample.

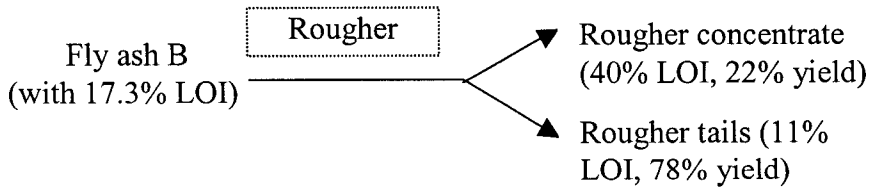

Figure 2. Test conducted to set approximated reagent requirements

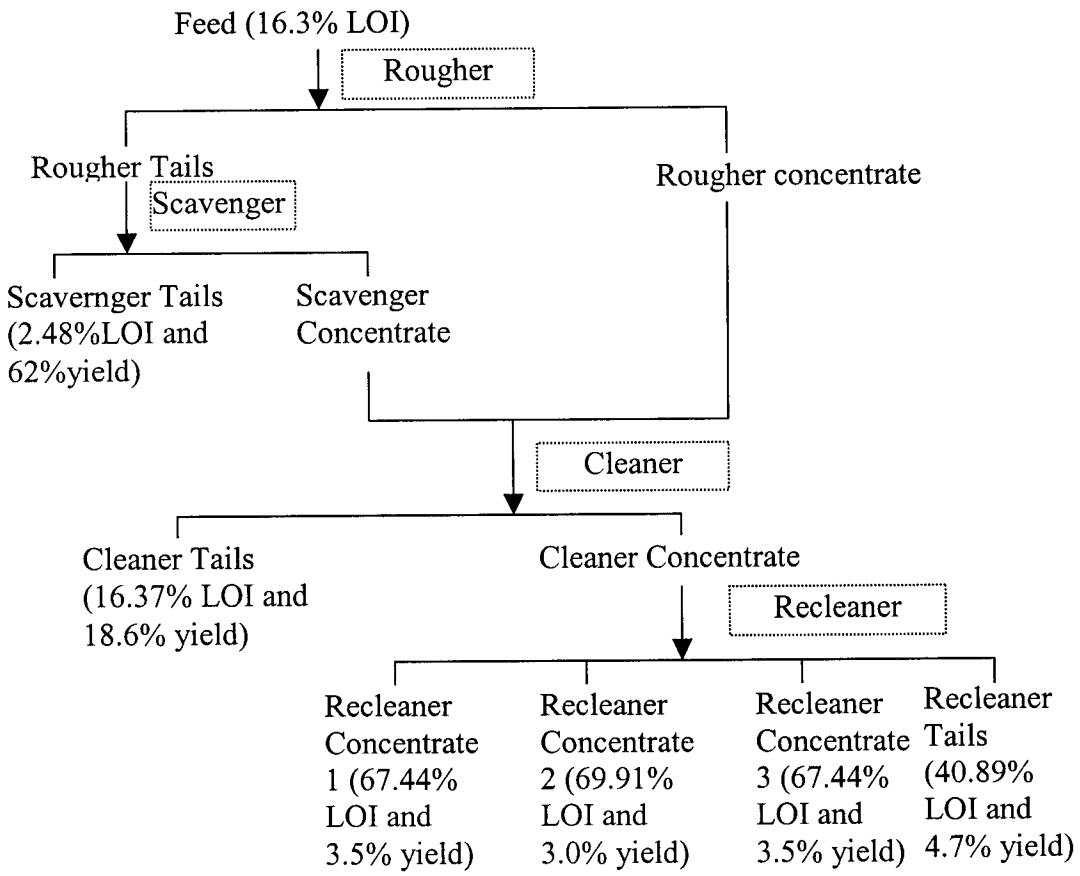

Figure 3. Froth flotation circuit variation test used to produce low ash carbon and low carbon ash.

The results from the circuit variation test also indicate that it will be difficult to produce a low ash carbon product from this material. The highest LOI of the carbon products was 69%--or 31% ash. The yield of this carbon product was also quite low at about 14.4%. Some ash is obviously present in this product, though the flotation products appeared to be quite black. The ash is either locked with the carbon or is in the form of cenospheres that were noted to be present in the floated material. It is currently being conducted a petrographical evaluation to determine the nature of the ash present prior to conducting additional flotation test work.

In addition, froth flotation tests were also conducted on the fly ash sample (LOI 58%) collected from the Penn State University research boiler, using a 2.5-liter WEMCO laboratory froth flotation cell. These tests were run with staged reagent additions to determine the floatability of the sample.

One hundred grams of the fly ash sample were wetted and placed into the laboratory cell where water was added to fill the cell and the slurry was mixed through the action of the flotation cell impeller. The slurry was mixed for approximately 2 minutes to ensure that the sample was sufficiently dispersed. Collector (fuel oil) was then added at a dosage of 62 microliters, which gives a dosage of about 1 lb of reagent per ton of fly ash. The collector was allowed to mix for two minutes prior to frother addition. For the first test, a commercial frother from American Cyanamid (now Cytec) was used. The dosage was 15 microliters or about 0.25 lb/ton. This was allowed to mix for one minute. The air was turned on and a lack of froth formation was observed. The air was turned off and additional reagents were added to attempt to float the carbon in the fly ash sample. After each dosage of collector or frother, the air was turned on and a lack of froth formation was observed. A total of 6 lb/ ton of collector and 1.5 lb/ton of frother was added in the first test, and further froth did not form.

A second test was performed with a different frother, that is a commercial frother from Nalco. This was tested to make sure that the frother quality was not an issue for the fly ash carbon separation. A total of 10 lb/ton of collector and 1 lb/ton of frother was added in stages to attempt to float the carbon from the fly ash. A froth did not form even with this high dosage of collector. Further anaylsis are presently being conducted, including based high carbon content, small particle size and high oxygen content.

4.2.2. Chemical cleaning

Table 1 lists the LOIs and porosities of the fly ash carbons before and after chemical cleaning. It can be seen that when the chemical cleaning was conducted at room temperature, the ash content can be reduced from 36.3wt% (precursor fly ash A) to 18.7wt% (A-W1). If the sample is subsequently treated again by chemical leaching, the

ash content can be further reduced to 1.1wt% (A-W2). This two-step process suggests that chemical demineralization is an effective method to produce a high purity carbon stream from fly ash. The same raw fly ash carbon, A, was also used to conduct the chemical cleaning experiment at 65°C to get the product A-W3. Upon increasing the temperature of the chemical cleaning process, a one-step treatment can directly reduce the ash content to 4.1wt% for A-W3. Furthermore, the produced cleaned sample A-W3, has similar surface area and pore size to those previously reported for the raw fly ash carbon, where the surface area and average pore diameter are 115m^2/g and 2.75nm, compared to 112m^2/g and 2.72nm for the original sample A. This may be related to the reaction residence time, which has been reduced to only 4 hr for the cleaning at 65°C, compared to the 2 days that were required for the cleaning process at room temperature. Finally, the long reaction residence time (2 days) resulted in a decrease of the surface area to 98m^2/g, and an increase of the pore size also to 2.94nm, probably due to the prolonged stirring that may have damaged the original pore structure due to attrition.

Table 1. Carbon content (LOI) and porosity of the parent fly ash carbon and their chemically cleaned counterparts.

Sample	Treat temp. °C	LOI wt%	SBET m^2/g	Vt ml/g	Average Pore Diameter, nm
A	-	63.7	112	0.0801	2.72
A-W1	Room	81.3	N/A	N/A	N/A
A-W2	Room	98.9	98	0.0718	2.94
A-W3	65	95.9	115	0.0789	2.75

The chemical cleaning process at 65°C shows that the ash content can be reduced to ~5wt%, and therefore, the resultant samples meet the ash content requirements of most applications, especially for activated carbons. A two-step chemical cleaning at room temperature can reduce the ash content to <1wt%, therefore meeting the more stringent ash requirements for certain carbon material applications, such as for the use of fly ash carbon as a replacement for calcined petroleum coke in carbon artifacts and anodes.

4.3. Production of premium carbon products

The high-purity carbon samples obtained from the above enrichment process were used to produce premium carbon products following the routes successfully developed in Phase 1 and 2.

4.3.1. Production of activated carbons

The fly ash carbon from coal-fired power plants can be used as precursor for the production of activated carbons, as demonstrated previously by the authors. As reported earlier, the one-step steam activation process can effectively convert fly ash carbons into activated carbons with surface areas as high as $540m^2/g$ [3]. However, as the activation time increases, the developing rate of micropore volume decreases, where micropore volumes are highly desired in commercial activated carbons. Therefore, a pretreatment process was designed and applied to fly ash carbons to improve their reactivity, and to modify the micropore structure of the resultant activated carbon [13]. Furthermore, a systematic parametric study on the pretreatment conditions has also been conducted.

4.3.1.1. The effect of activation time on steam activated carbons

Figure 4 shows the N_2-77K isotherms for the steam activated carbons produced from the unburned carbon B with different activation time. Figure 4 shows that with increasing activation time, the isotherms change from Type 1 for 60 minutes activation, B-60, into Type 4 for 180 minutes activation, B-180. For the isotherm of B-60, the adsorbed volume increases rapidly at low relative pressure, while at higher pressure, the adsorbed volume increases very slowly, which implies that most of the pores in the samples are micropores. In contrast, for the isotherm of B-180, the adsorbed volume keeps increasing progressively with the relative pressure, and there is a distinct hysteresis loop in the isotherm, which indicates that the sample is mainly mesoporous.

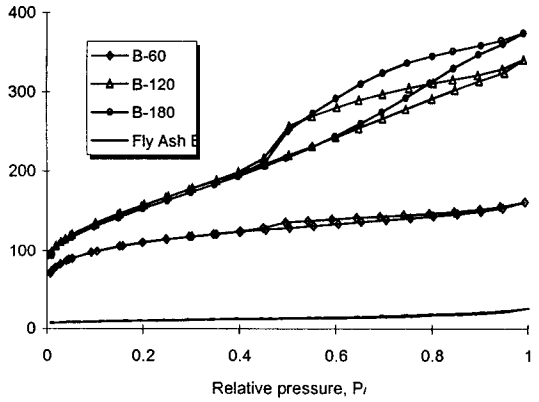

Figure 4. N_2-77K isotherms of steam activated carbons produced from unburned carbon B and the parent sample.

The solid yields and surface areas are listed in Table 2 for the parent and steam activated samples. After 1 hour activation, the resultant activated carbon surface area was $332m^2/g$. As expected, when the activation time increased to 2 hours, the solid yield decreased, while the total surface area and pore volume increase to $540m^2/g$ and 0.500ml/g, respectively. When the activation time was increased to 3 hours, the surface area was similar to that for 2 hours, but the pore volume increased to 0.556ml/g, suggesting a widening of the porosity.

Table 2. Solid yields and surface areas for the parent and stem activated carbons produced from unburned carbon in fly ash.

Samples	Activation time hr	Solid yield wt%	SBET m^2/g	Vt ml/g
B	-	-	40	0.03
B-60	1	73.2	332	0.237
B-120	2	34.8	540	0.500
B-180	3	30.6	534	0.556

4.3.1.2. The effect of KOH pretreatment on unburned carbon activation

Chemical pretreatment with KOH was performed to increase the reactivity of the unburned carbon. A known amount of KOH was loaded on the unburned carbon followed by steam activation. The isotherms of resultant activated carbons are shown in Figure 5. With 1.5wt% KOH, the resultant activated carbon, B-KOH-1.5, has an isotherm with similar shape to that of B-60, although it has larger adsorbed volume, which suggests a similar high microporosity as B-60.

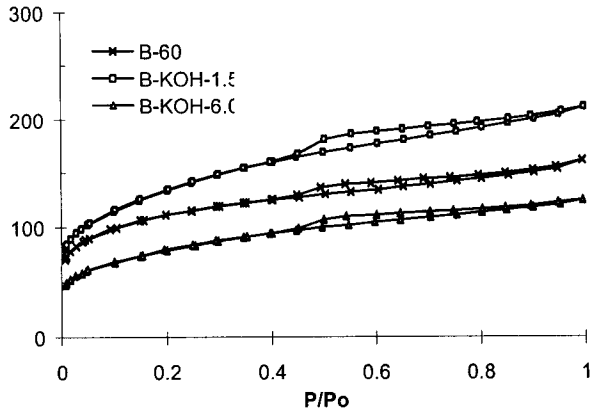

Figure 5. N_2-77K isotherms of activated carbons made from the unburned carbon B loaded with KOH.

Table 3 lists the solid yields and surface areas for the parent and activated carbons produced from unburned carbon in fly ash by KOH pretreatment. With only 1.5wt% KOH, compared to that without pretreatment B-60, the surface area of AC can increase 35.5% ($450m^2/g$ vs. $332m^2/g$). However, with further increase in the KOH load up to 6wt%, the surface area decreases. This may be due to the limited amount of active sites on the surface of unburned carbon, which can adsorb KOH. Hence, with higher burn-off, the gasification reaction still happens on the same active sites, resulting in a widening of the exist pores.

Table 3. Solid yields and surface area for the parent and activated carbons produced from unburned carbon in fly ash by KOH pretreatment.

Sample	KOH load wt%	Activation time	Solid yield wt%	S_{BET} m^2/g	Vt ml/g
B-KOH-1.5	1.5	1	61.7	450	0.316
B-KOH-6.0	6.0	1	42.3	427	0.359

4.3.1.3. The effect of gas pretreatment on unburned carbon activation

During this reporting period, the samples were pretreated for 2 to 4 hours at 300°C to 400°C prior to 1 hour steam activation at 850°C. The N_2 isotherms of the resultant activated carbon are shown in Figure 6. For the purpose of comparison, the sample with no pretreatment is also included in Figure 6. The activated carbons prepared after pretreatment at 300°C have similar isotherm shapes to that of the sample without pretreatment, but they have much larger adsorbed volume, suggesting a similar microporosity structure, but a higher surface area and total pore volume. However, when the pretreatment time is extended to more than 3 hours, the more open knee of the isotherm at lower relative pressures indicates a broader pore size distribution with larger micropores and some mesopores.

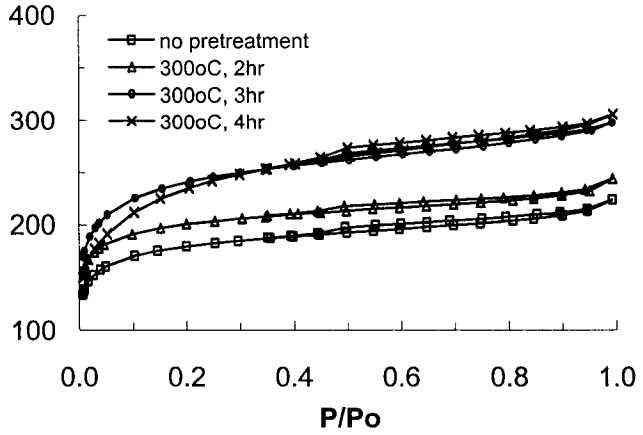

Figure 6. N_2-77K isotherms of activated carbons made from the fly ash carbon (FA1) pretreated at 300°C and the parent sample activated without pretreatment.

The surface areas and pore volumes for the activated carbons produced with or without pretreatment at 300°C and 400°C are listed in Table 4. Although all the activated carbons were made using the same activation conditions (activation temperature and time are 850°C and 1 hour, respectively), the pretreatment can increase the surface area of the resultant activated carbon up to ~60% (from 534m^2/g without pretreatment to 854m^2/g with 2 hour pretreatment at 400°C) compared to that of the sample without pretreatment. In addition, the pretreated samples can also keep similar average pore size (2.47nm vs. 2.44nm).

Table 4. Surface areas and pore volumes of activated carbons from fly ash carbon

Pretreatment		Activation		St	Vt	Average pore diameter
Temp. °C	Time hr	Temp. °C	Time hr	m^2/g	ml/g	nm
No		850	1	534	0.329	2.44
300	2	850	1	591	0.359	2.41
	3	850	1	724	0.447	2.45
	4	850	1	733	0.457	2.56
400	2	850	1	854	0.535	2.47
	3	850	1	841	0.556	2.60

For extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores and an increase of the total pore volumes (Table 4). For the samples pretreated at 300°C, the surface area only increases from 724m^2/g for 3 hours pretreatment to 733m^2/g for 4 hour pretreatment, while the average pore diameter increases to 2.56nm from 2.45nm, and the total pore volumes are enlarged to 0.457ml/g from 0.447ml/g. Similarly, for the samples pretreated at 400°C, the extended pretreatment time also decreases the surface area, from 854m^2/g for 2 hr pretreatment to 841m^2/g for 3 hr pretreatment. Therefore, it can be concluded that for the lower pretreatment temperature, the optimum pretreatment time is longer than that of the higher temperature pretreatment (3 hour for 300°C pretreatment vs. 2 hours for 400°C pretreatment).

Figure 7 compares the surface areas and pore volumes for the activated fly ash carbon samples pretreated for 3 hours at different temperature (300, 350, and 400°C) prior to activation. It can be seen that with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon.

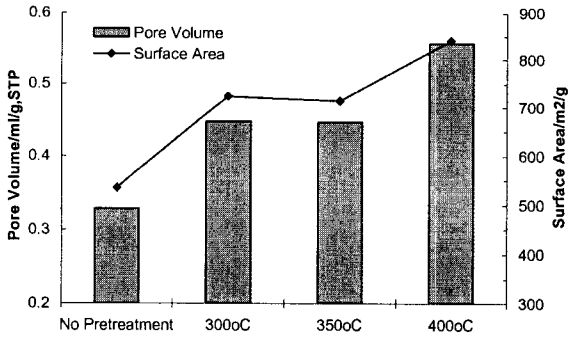

Figure 7. Pore volume and surface area of activated carbons made from FA1 with 3 hours pretreatment at different temperatures.

4.3.2. Characterization of fly ash carbon towards its potential use as precursor for carbon artifacts

Table 5 lists the elemental analysis of both unburned carbon and the petroleum coke investigated in this work.

Table 5. Elemental analysis for the unburned carbon and petroleum coke.

Sample	%C(daf)	%H(daf)	%N(daf)	%S(daf)	%O(daf)	H/C (*10^{-3})
Unburned carbon	97.7	0.02	1.40	0.94	<0.01	2.46
Petroleum coke	96.2	0.02	0.57	3.42	<0.01	2.49

The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows that its carbon content is as high as 97.7% and hydrogen content is as low as 0.02%, giving an H/C atomic ration well below 0.01. These values are comparable with conventional calcined petroleum coke, that are also shown in Table 5. Furthermore, the sulfur content of the unburned carbon is

significantly lower that that of petroleum coke, 0.94% vs. 3.42%. This is indeed a very attractive characteristic, since the undesired increasing sulfur concentrations in petroleum coke are known to mar the carbon products used in the aluminum and steel industries.

Table 6 lists the surface area and total pore volume determined from the N_2 isotherm at 77K, and the density for unburned carbon compared to that of the petroleum coke. The density of the unburned carbon is somewhat lower than the petroleum coke (1.59 vs. 1.89g/ml), probably due to its higher surface compared to that of the petroleum coke (14.15m^2/g vs 2.01-4.85m^2/g). From the SEM image (Figure 8), it can be seem that the unburned carbon is generally solid carbon with some macropores, probable formed during the rapid devolatilization process experienced in the combustor.

Table 6. N_2-77K BET surface areas (S_{BET}) and total pore volume (V_t) and densities of the unburned carbon and the petroleum coke.

Sample	S_{BET}, m^2/g	V_t, ml/g	Density, g/ml
Unburned carbon	14.15	0.013	1.59
Petroleum coke	4.85	0.008	1.89

During the heat treatment experienced in the combustor by the unburned carbon, some coal particles have gone through a softening stage and have formed ordered carbon forms (anisotropic coke), while others have formed random configurations (isotropic coke), as illustrated in the optical micrographs shown in Figures 9-11 (horizontal field width is 220μm). The ratio of anisotropic over isotropic coke for this particular sample is about 7/1. The rapid heat treatment experienced in the combustor creates some porosity in the unburned carbon, and therefore, its surface area is larger than that of petroleum coke (Table 6). Figure 9 shows a typical large anisotropic mosaic texture derived from the carbonization of the vitrinite fraction. Figure 10 shows a typical isotropic material derived from coal inertinite trapped in an anisotropic matrix derived from the carbonization of vitrinite. Finally, Figure 11 shows a large particle of inertinite (macrinite) trapped in the anisortropic amatrix of the unburned carbon. The presence of

isotropic and anisotropic textures is also characteristic of petroleum coke, where a given ratio of anisotropic over isotropic coke is required for different applications [16].

Figure 8. SEM image of the unburned carbon.

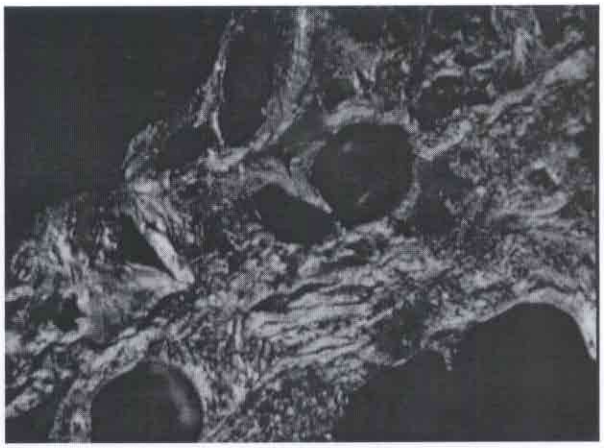

Figure 9. A typical anisotropic mosaic texture in unburned carbon.

Figure 10. A typical isotropic material trapped in an anisotropic matrix in unburned carbon.

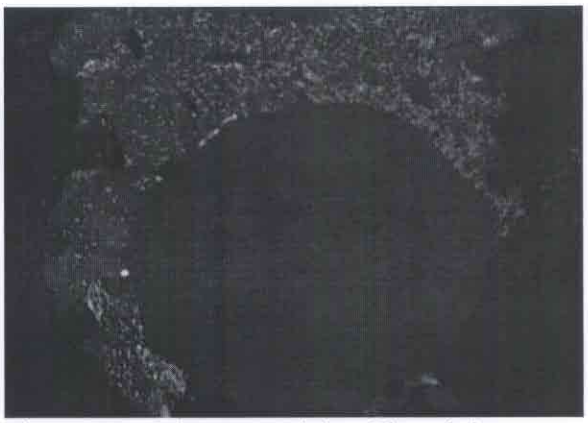

Figure 11. A large particle of inertinite (macrinite) trapped in the anisotropic matrix of unburned carbon

5. CONCLUSIONS

The present work has evaluated the cleanability of fly ash carbons from coal-fired power plants towards their utilization as feedstocks for activated carbons.

The work reported in this report has demonstrated the feasibility of the application of froth flotation for the separation of power plant fly ash into carbon and ash stream. From a fly ash sample collected from Shawville station with a carbon content or LOI (loss-on-ignition) of 17%, it was possible to obtain a carbon stream with LOI of 70% and ash stream with LOI of 2.5% by applying froth flotation. As expected, the recovery yields are significantly reduced as the purity of these two streams was optimized. Chemical digestion has also been applied to a fly ash sample with an ash content of ~37wt%, and the resultant fly ash carbon stream has an ash content of only ~1wt%. Furthermore, the chemical cleaning process was also conducted at 65°C, where the ash content can be reduced to ~5wt% after only 4 hours. The resultant cleaned fly ash carbons meet the ash content requirements of most carbon materials applications.

Following the previous work that demonstrated the ability of unburned carbon from coal combustion by-products to generate activated carbons by steam activation, the work reported here has also further investigated and optimized two kinds of pretreatment process to promote the microporous structure of the resultant activated carbon. After 2 hours steam activation, activated carbons with surface area up to 540m^2/g have been generated from the unburned carbon in combustion waste. Pretreatment of the unburned carbon with 1.5wt% KOH, resulted in a 35.5% increase of the surface area of the resultant activated carbon, while retaining relatively high solid yields. For the second pretreatment method, all the different pretreatment conditions studied in the report promote the porosity of resultant activated carbons, where the surface area increases ~11-60%. With increasing pretreatment time, there is an increase in the porosity (surface area and pore volume) of the resulting activated carbons. However, for extended pretreatment periods (4 hours for 300°C and 3 hours for 400°C), there is no further increase of the surface area, but rather a widening of the existent micropores, and an increase of the total

pore volumes. Furthermore, with increasing pretreatment temperature, both the surface area and pore volume increase for the resultant activated carbon. The optimum pretreatment conditions found during the current reporting period are 400°C and 2 hr, where the resultant activated carbon has a surface area of 854m^2/g and a pore volume of 0.56ml/g, which are comparable to those values reported for commercial activated carbons.

In addition, the work reported here also included the characterization of fly ash carbons. The unburned carbon has been treated at temperatures well above 1200-1300°C in the combustor, and therefore its elemental analysis shows a very high carbon content (97.7%), and conversely, low hydrogen content (0.02%), that are comparable with values also reported for conventional calcined petroleum coke. Furthermore, the sulfur content of the unburned carbon is significantly lower than that of petroleum coke, 0.94% vs. 3.42%. In contrast, the density of unburned carbon is somewhat lower than for petroleum coke, probably due to its surface area, that is created by the rapid heat treatment experienced in the combustor by the unburned carbon. Furthermore, both the unburned carbon and the petroleum coke present isotropic and anisotropic textures, where a given ratio of anisotropic over isotropic coke is required for different applications.

This project has a no-cost extension till May 31, 2002. An addendum to the present report summarizing the work conducted during the remaining period will be submitted after the project ending date.

6. PROJECT RELEVANCE TO THE COAL INDUSTRY

The rise in unburned carbon concentration in coal combustion fly ashes may lead to the demand for the coal utility industry to begin offsetting coal with natural gas, or require additional coal cleaning to remove the ash prior to combustion. Both alternatives would clearly compromise the coal industry. Hence, the implication of this research program is to turn unburned carbon containing fly ash from a liability into an asset for the coal industry.

The U.S. energy industry requires a green chemistry and engineering solution that can guarantee a long-term source of energy by simultaneously reducing emissions and byproduct waste streams. This can be achieved by installing low-NO_x burners, which have been proven to efficiently reduce NO_x emissions, coupled with strategies to manage the associated increase of byproduct streams. Accordingly, the recovery and recycling of energy byproducts can bring enormous economical and environmental benefits to the U.S. energy industry and to society at large. However, the implementation of Clean Air Act Regulations is potentially detrimental to the marketability of ash, in the sense that more unburned carbon is present in the ash, with the subsequent rise in waste streams to follow. Several technologies have been successfully developed to recover and separate the unburned carbon from the ash. These technologies can be divided into wet (froth flotation) and dry (triboelectrostatic) processes, and they can give inorganic ash concentrates with purities that meet the requirement for the cement industry, as well as carbon concentrates with purities of 85% and above. However, only a few power plants have installed a beneficiation process on their sites. One of the main reasons for this is the low value of the resultant separation products, since one ton of "clean" fly ash is generally sold for as little as $10, and the unburned carbon concentrated stream is simply rerouted to the combustor. However, the economics of this process can be significantly enhanced if both separated materials can be used as precursors for high-value products. Accordingly, this research program has developed novel routes for the commercial use of unburned carbon present in fly ash as a precursor for premium carbon materials, like activated carbons.

To conclude, the benefits of this research program can be summarized as follows: (i) the coal industry will continue being the main provider to the utility industry, where currently over 900 million tons of coal are sold annually; (ii) the carbon industries, such as those producing activated carbons, will have cost-effective and novel precursors; and (iii) this program prevents pollution at its source by simultaneously reducing NOx emissions and byproduct waste streams, including unburned carbon and ash, and will therefore have a vast benign environmental impact.

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