Development of Management Options for Biomass Combustion By-Products

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INTRODUCTION

Combustion of biomass fuels either alone or in conjunction with coal has the potential to result in by-products with different characteristics than those from 100% coal or other fossil fuels. Coal–biomass by-products are expected to be appropriate for some utilization applications, but the primary issue of cocombustion of biomass with coal relates to fly ash use as a mineral admixture in concrete. The American Society for Testing and Materials (ASTM) has an existing standard specification for 100% coal fly ash for use in concrete. Some coal–biomass fly ash has been shown to meet the technical specifications noted in this standard (C618); however, the definition of fly ash in the standard indicates that it refers to fly ash produced only from 100% coal as the fuel. There is an ongoing debate whether ASTM should modify the definition of fly ash or develop an alternate standard for cocombustion fly ash. The ASTM Subcommittee C 9.24 has decided to postpone any action until technical data have been presented to support a position in this debate. In addition, coal–biomass by-products may have applicability in other applications, but this has not been well investigated. The Energy & Enviromental Research Center (EERC) contines work in this area to support ASTM activities in assembling adequate data that will provide a baseline from which the subcommittee can proceed with confidence.

Coal combustion by-product (CCB) utilization has been an area of research at the EERC for over 20 years. Coal–biomass and biomass by-products require similar evaluation before they can be managed effectively. The EERC is using the experience and facilities developed through its ongoing coal ash research to develop a program to characterize a limited number of coal–biomass ash samples for properties that are important in facilitating by-product management decisions, especially as they relate to use in concrete. One part of this effort is to develop a database of the characterization data already available at the EERC and generated under this effort. This effort is modeled after the very successful Coal Ash Properties Database, which grew from a simple spreadsheet cataloging both physical and chemical parameters of fly ash collected from both full-scale combustion units and bench-/pilot-scale tests conducted in EERC test facilities. By putting all of the information in a single place, researchers were able to study, sort, and compare large data sets to look for trends and relationships. When the coal–biomass and biomass by-product characterization data are in a single place as a research

tool, it will facilitate improved by-product management and comparisons with existing CCB data. This project will investigate the technical appropriateness of coal–biomass and biomass combustion for utilization scenarios.

EXPERIMENTAL

The experimental plan comprises the following tasks:

Task 1 – Literature Review, Assessment, and Assembly of Annotated Bibliography. A search was performed to obtain additional documentation on combustion and gasification of biomass fuels, the resulting by-products, and the management of those by-products. An annotated bibliography was prepared with 25 references.

Task 2 – Sample Collection and Generation. Samples previously collected from EERC bench- and pilot-scale combustion tests were included in this subtask, however, some samples were not available in adequate quantity to perform all testing. By-products from full-scale coal–biomass, biomass combustion, and gasification tests were obtained.

Task 3 – Develop Laboratory Data. Samples of coal–biomass fly ash, biomass ash, and gasification ash were evaluated for chemical composition and standard physical/engineering properties key for utilization. Bulk major chemical composition of fly ash provides an indication of chemical reactivity of fly ash in concrete systems, including the potential for the fly ash to contribute to concrete failure mechanisms such as alkali–silica reactivity (ASR) and sulfate attack. Particle size, strength development, and expansion tests are also key to determining the appropriateness of fly ash for use as a mineral admixture in concrete. These tests also provide information that relate to nonconcrete utilization applications. Engineering testing parameters consisted of particle fineness, evaluation for use in concrete, ASR, and sulfate resistance. Testing for particle fineness was performed using a Malvern particle analyzer.

Task 4 – Develop a Characterization Database. A large amount of analytical data from coal–biomass fuels and ash exists at the EERC. All ash-related data were collected and inventoried. A very simple form of database was started with the physical and chemical parameters available.

Task 5 – Reporting and Information Dissemination. Information dissemination for the results based on coal–biomass fly ash involves communication with ASTM C 09 Committee on Concrete and Concrete Aggregates, including attendance at a minimum of one committee meeting to summarize assembled results.

Engineering Parameters – Background

Fly ash being sold for admixture with portland cement in concrete typically must meet the specifications contained in ASTM C618 – Standard "Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Concrete. Since valuable sales contracts can be lost if test results indicate that a fly ash does not meet these specifications, it is important for utility companies and ash marketers to understand the inherent variability

associated with tests used to evaluate fly ash. It is also important to be able to estimate the variability of C618 test results when they affect the marketability of fly ash. For example, if the test results indicate, by a narrow margin, that a fly ash fails to meet a particular specification, a question may arise as to whether the ash is actually unacceptable or that the test result is possibly inaccurate. To answer this type of question, the intralaboratory standard deviations can be used to estimate the probability that a single test result has incorrectly indicated that a fly ash does not meet a particular specification. If that probability is high, it may be prudent to have the test repeated to verify the result.

The ASTM is probably the most widely recognized and used national standards-setting organization in the United States for engineering-related materials and testing. The ASTM C618 specification is the most widely used because it covers the use of fly ash as a pozzolan or mineral admixture in concrete. The three classes of pozzolans are Class N, Class F, and Class C. Class N is raw or calcined natural pozzolan such as some diatomaceous earths, opaline cherts, and shales; tuffs, volcanic ashes, and pumicites; and calcined clays and shales. Class F is pozzolanic fly ash normally produced from burning anthracite or bituminous coal. Class C is pozzolanic and cementitious fly ash normally produced from burning lignite or subbituminous coal. Table 1 shows the chemical and physical requirements listed in the ASTM C618 specification.

Alkali–Silica Reactivity

ASR is a reaction between alkali hydroxides in portland cement and siliceous phases present in the admixtures and aggregates composed of SiO_2. Problems with expansion arise when soluble silica reacts with the alkalies, forming an alkali−silica hydrate gel. In concrete, CaO is associated with silica and forms a nonswelling calcium silicate hydrate gel during hydration as a key reaction related to cementation.

Fly ash is often added to mitigate expansion due to ASR. Current thought on the leading mechanisms by which fly ash controls expansion is that the fly ash dilutes the alkali content in the cement, removes some of the alkalies from the pore solution by binding them into CaO–silica hydrate gels, and reduces the concrete permeability and diffusivity when silica reacts with the $Ca(OH)_2$ produced by the hydration of the cement to form calcium silicate hydrate. Since the calcium silicate hydrate takes up more space than the $Ca(OH)_2$, the pore systems become finer and less continuous. The reduced porosity limits the ability of the alkalies to migrate and, therefore, reduces the ability of alkali−silica gel to form.

The samples tested for ASR are listed in Table 2. Several of the samples tested for ASTM C618 analyses were not included because of the insufficient amounts of available material. The method used for ASR evaluation was ASTM C441 – Effectiveness of Mineral Admixtures or Ground Blast-Furnace Slag in Preventing Excessive Expansion of Concrete Due to the Alkali–Silica Reaction. This test method covers the determination of the effectiveness of mineral admixtures or slag in preventing the excessive expansion caused by reaction between aggregates and alkalies in

Table 1. ASTM Specification C618-92a Chemical and Physical Specifications

	Mineral Admixture Class		
	N	F	C
Chemical Requirements			
Silicon Dioxide, Aluminum Oxide, Iron Oxide (SiO_2 + Al_2O_3 + Fe_2O_3), min. %	70	70	50
Sulfur Trioxide (SO_3), max. %	4.0	5.0	5.0
Moisture Content, max. %	3.0	3.0	3.0
Loss on Ignition (LOI), max. %	10.0	6.0[a]	6.0
Available Alkalies as Na_2O, max. %[b]	1.5	1.5	1.5
Physical Requirements			
Fineness, max. % retained on 325-mesh sieve	34	34	34
Strength Activity Index with Portland Cement			
7-day, min. % of control	75[c]	75[c]	75[c]
28-day, min. % of control	75[c]	75[c]	75[c]
Water Requirement, max. % of control	115	105	105
Autoclave Expansion, soundness, max. %	0.8	0.8	0.8

[a] The use of Class F pozzolan with up to 12% LOI may be approved by the user if either acceptable performance records or laboratory test results are made available.

[b] Applicable only when specifically required by the purchaser for mineral admixture to be used in concrete containing reactive aggregate and cement to meet a limitation on the alkali content.

[c] Meet the 7- or 28-day strength activity index will indicate specification compliance.

Table 2. Biomass Samples Tested for ASR

FMRL[a] No.	CARRC[b] No.	Description
02-456	02-052	Cocombustion Fly Ash, Weston, 4/19/99
02-826	02-066	Minnesota Power Biomass Fly Ash, Unit 2
02-1108	02-075	TVA Colbert Fossil Plant 3% BACA/Woodwaste
03-072	03-001	
03-073	03-002	
03-074	03-003	

[a] Fuels and Materials Research Laboratory.

[b] Coal Ash Resources Research Consortium.

portland cement mixtures. The evaluation is based on the expansion developed in mortar bars by a combination of high-alkali portland cement and a mineral admixture, made with reactive aggregates (Pyrex glass), during storage under prescribed conditions of testing.

Sulfate Resistance

It is quite common in cold weather climates for salts to be applied to concrete surfaces to reduce ice accumulation and skidding. Oftentimes, these salts are blended with sands for distribution. Concrete surfaces, particularly bridge decks, can be hard hit by this sulfate attack. If the exposed section of highway is not extensive in length, liquid sealers can be applied to the freshly hardened concrete surface. However, it would be cost-prohibitive to use expensive surface treatments for extensive miles of concrete. Testing concrete for sulfate resistance is designed to simulate field conditions whereby these sulfate environments can be evaluated for their effects on concrete and/or mortar mixtures.

The biomass samples tested for sulfate resistance are the same as those evaluated for ASR, which are listed in Table 2. The standard test method used here for evaluating mineral admixtures for sulfate resistance is ASTM C1012 – Length Change of Hydraulic-Cement Mortars to a Sulfate Solution. This test method covers the determination of length change of mortar bars immersed in a sulfate solution. It provides a means of assessing the sulfate resistance to be expected of concretes and mortars made using portland cement, blends of portland cement with pozzolans or slags, and blended cements. The standard exposure solution used in this test method contains a 5% concentration of sodium sulfate (Na_2SO_4). Other sulfates and concentrations are allowed in this procedure, but sodium sulfate is the one prescribed in the methodology.

ASTM C1012 also allows for different types of cements to be used in the mortar mixtures. The most commonly used cement in this procedure is Type V, which is designed to be resistant to sulfate solution attack. Other types of cements allowed are Type II, which is a standard type normally used in every concrete application, and blended cements, commercially available cements that have already been blended with coal-combusted fly ash.

TASK RESULTS AND DISCUSSION

Task 1 – Literature Review, Assessment, and Assembly of Annotated Bibliography

The literature search was finalized with completion of a formal annotated bibliography. The annotated bibliography will be included in full in the final subtask report as an appendix. The annotated bibliography contains 25 citations and associated summaries. The complete annotated bibliography can be found at the EERC website at www.undeerc.org.

Task 2 – Sample Collection and Generation

Sample collection was a greater effort for this subtask than was originally anticipated. The level of interest in the characteristics of coal–biomass ash expressed by utility ash managers and ash marketers had indicated that coal–biomass ash samples would be relatively easy to obtain. This was not the case. Researchers worked within the EERC to assess the existing catalogue of EERC biomass-related ash samples. There were numerous biomass ash samples catalogued; however, very few coal–biomass ash samples were available from EERC bench- and pilot-scale

combustion facilities or full-scale facilities. In most cases, the sample size was extremely limited and inadequate for the testing required to evaluate the ash for appropriateness as a mineral admixture in concrete. Samples were requested from utilities that had performed coal–biomass combustion tests, were planning coal–biomass combustion tests, and regularly used biomass as a cofuel. The samples obtained and used in most of the laboratory testing are noted in Table 3, and all were obtained from a full-scale combustion system.

Table 3. Sample Description

Sample No.	Coal % and Type	Biomass % and Type	System Description
02-052	95% PRB subbituminous	5% waste paper	Hot-side ESP
02-053	77% subbituminous	23% sunflower hulls	Baghouse
02-053 (sieved)	77% subbituminous	23% sunflower hulls	Baghouse
02-054	77% subbituminous	23% sunflower hulls	Multicyclone
02-066	60% subbituminous	40% unidentified	
02-075	97% eastern bituminous	3% BACA/wood waste	
03-001	92% bituminous	8% furniture manufactured waste	Low-NO$_x$ burner/ESP
03-002	92% bituminous	8% furniture manufactured waste	Low-NO$_x$ burner/ESP
03-003	92% bituminous	8% furniture manufactured waste	Low-NO$_x$ burner/ESP

Task 3 – Develop Laboratory Data

The engineering testing program consisted of ASTM C618 for chemical and physical analyses, particle-size distribution, sulfate resistance, and alkali reactivity. The results of the ASTM C618 testing are contained in Table 4. The wide variance in biomass samples has resulted in a broad spectrum of chemical and physical characteristics according to ASTM C618 procedures. The total silicon, aluminum, and iron oxides ranged from 27.62% up to over 90%. The total oxides for these three elements determine the dividing line for classification of coal combustion fly ashes according to ASTM C618. The differences were reflected in either higher levels of calcium

Table 4. ASTM C618 Analyses of Biomass Samples

Chemical Parameter Composition, %	Sample 02-052	Sample 02-053	Sample 02-054	Sample 02-066	Sample 02-075	Sample 03-001	Sample 03-002	Sample 03-003
Silicon Dioxide, SiO_2	33.23	30.05	35.00	44.71	55.51	53.83	55.85	54.25
Aluminum Oxide, Al_2O_3	19.42	18.84	16.80	8.23	25.09	28.79	28.75	28.92
Iron Oxide, Fe_2O_3	5.79	1.28	2.19	3.80	7.69	6.87	6.23	6.01
Total $SiO_2+Al_2O_3+Fe_2O_3$	58.44	50.17	53.99	56.74	88.29	89.49	90.83	89.18
Sulfur Trioxide, SO_3	2.22	6.07	2.41	2.95	0.43	0.37	0.23	0.62
Calcium Oxide, CaO	25.25	19.83	14.6	28.01	4.55	3.30	2.32	4.02
Moisture Content	0.03	5.23	0.55	0.34	0.23	0.12	0.13	0.12
Loss on Ignition	0.24	57.78	12.14	8.49	7.80	11.08	8.77	11.98
Available Alkalies	2.03	0.50	1.03	1.97	0.73	1.01	0.88	0.98
Magnesium Oxide, MgO	6.17	8.27	4.80	2.59	1.72	1.29	1.16	0.86
Sodium Oxide, Na_2O	3.85	0.36	0.19	2.90	1.45	0.76	0.74	0.88
Potassium Oxide, K_2O	0.41	11.28	2.24	4.51	1.61	2.40	2.52	1.96
Physical Parameters								
325-mesh Fineness, %	19.18	47.52	54.84	65.22	31.58	3.34	1.20	2.20
7-day Activity Index, %	95	78	66	66	75	102	86	90
28-day Activity Index, %	85	70	61	62	76	103	100	98
Water Requirement, %	99	128	120	112	103	101	105	103
Autoclave Expansion, %	0.0	0.02	0.02	0.11	0.0	-0.03	-0.02	-0.02
Specific Gravity	2.72	2.30	2.30	2.55	2.21	2.32	2.32	2.29

oxide or LOI. Higher-than-normal levels of magnesium, sodium, and potassium oxide can also be found in the biomass samples. Some samples would not meet the ASTM requirements for use as partial cement replacement in concrete due to high levels of LOI. The specification calls for a LOI not to exceed 6%. Most of the biomass samples have LOI measurements exceeding 10%.

There are two physical parameters, according to ASTM C618, which closely relate to one another. They are the 325-mesh fineness and the cement activity index (CAI). The fineness procedure is a wet sieve analysis that determines the amount of ash retained on a 325-mesh (45 μm) screen. The maximum allowable retainment is 34%. The CAI is a ratio, expressed as a percent, between the compressive strength of a mortar containing cement and ash to that of a mixture containing only cement, also referred to as a "control." The minimum requirement here is for the test mixture to have a cement activity index of 75%. The biomass ashes had finenesses ranging from 1.2% to over 54%. In most instances, the activity index decreases as the fineness increases. An ash sample needs to only surpass the 7- or the 28-day activity index to be considered passing the CAI procedure. However, in instances where a biomass sample passed only one of the CAI specifications, there were other characteristics exceeding specification limits which would prohibit the material to be used as a commercial product for partial replacement of cement in concrete. In most cases, other selections of utilization would need to be considered.

CARRC Samples 03-001 thru 03-003 resulted in high CAI values. This is most likely due to the extremely low retainment on the 325-mesh sieve. The values obtained here are exceedingly low when compared to more traditional precipitator coal ashes. The LOI levels for these three samples are too high for consideration as an admixture additive in concrete. Assuming the utilization market is economically feasible, the recommendation would be to classify these samples to lower the LOI contents. Air classification has been used in this manner to benefit several sources of coal combustion ash and is commercially available.

The biomass sample that would make the best candidate for use as partial cement replacement in concrete would be CARRC Sample 02-052. All physical and chemical parameters, with the exception of the available alkali, were successfully met for specification limits. However, considering that the final available alkali value exceeded the specification by a relatively small amount and the fact that this procedure is no longer listed in ASTM C618 specifications, the biomass sample would still be a good candidate in a portland cement concrete application.

Testing for ASR requires the fabrication of a control test mixture that does not incorporate the usage of a mineral admixture. From the calculated data, the reduction of mortar expansion is derived. This ASTM test procedure has been performed several times in the past by the EERC. These historical test data are given in Table 5 for comparison purposes to the biomass samples. The test results for the biomass samples are given in Table 6.

Table 5. Previous Testing at the EERC for ASR

Sample description	Average Length Expansion,%	Reduction of Expansion,%
Control (1992)	0.406	—
Control (1994)	0.379	—
Control (1996)	0.372	—
Class C Fly Ash (1992)	0.165	59.3
Class C Fly Ash (1994)	0.157	58.5
Class C Fly Ash (1996)	0.166	55.4

With the exception of Sample 02-066, all the selected biomass samples performed very well for this test procedure. Sample 02-066 was the only sample that produced expansion results higher than those exhibited by the control sample. The conclusion can be made that, with the exception of the aforementioned sample, all of the biomass materials had acceptable reduction of expansion results.

Testing for sulfate resistance also requires the fabrication of a control mixture containing no mineral admixture. The EERC also has performed this procedure several times in past years using different cements, so this information is used here for comparison purposes. The biomass samples were evaluated using Type V cement, so only historical EERC test data on mixtures using this source are included in Tables 7-9. The results of the biomass testing are shown in

Table 10. According to ASTM C595, the maximum allowable expansion at 180 days (6 months) is 0.10%.

Table 6. Results of Testing Biomass Samples for ASR

Sample description	Average Length Expansion, %	Reduction of Expansion,%
Control (2003)	0.229	—
CARRC 02-052	0.125	45.4
CARRC 02-066	0.317	−38.4
CARRC 02-075	0.075	67.2
CARRC 03-001	0.059	74.2
CARRC 03-002	0.047	79.5
CARRC 03-003	0.063	72.5

Table 7. Average Length Expansions Due to Sulfate Resistance Using Type V Cement (1991)

Specimen Age	Control	Class C Ash #1	Class C Ash #2	Class F Ash
1 week	0.012	0.014	0.014	0.012
2 weeks	0.015	0.016	0.018	0.014
3 weeks	0.016	0.016	0.017	0.015
4 weeks	0.014	0.017	0.022	0.015
8 weeks	0.019	0.022	0.025	0.021
13 weeks	0.030	0.025	0.028	0.022
15 weeks	0.034	0.031	0.040	0.034
4 months	0.039	0.034	0.045	0.035
6 months	0.042	0.036	0.071	0.040

Because of delays in sample preparations for this standard test method, there was insufficient time to evaluate the test samples for the entire prescribed length of exposure. Specimens were only exposed to sulfate, and subsequently measured for length, for 2 months at the time of writing of this report. The testing will eventually be performed for the prescribed 6 months of exposure. However, those end results will not be available in this document.

Table 8. Average Length Expansions Due to Sulfate Resistance Using Type V Cement (1994)

Specimen Age	Control	Class C fly ash	Class F fly ash
1 week	0.008	0.006	0.004
2 week	0.010	0.011	0.009
3 week	0.012	0.012	0.010
4 week	0.014	0.015	0.011
8 weeks	0.016	0.016	0.018
13 weeks	0.023	0.026	0.027
15 weeks	0.029	0.028	0.028
4 months	0.028	0.027	0.027
6 months	0.035	0.033	0.032

Table 9. Average Length Expansions Due to Sulfate Resistance Using Type V Cement (1996)

Specimen Age	Control	Class C fly ash
1 week	0.001	0.003
2 weeks	0.008	0.008
3 weeks	0.011	0.011
4 weeks	0.010	0.014
8 weeks	0.015	0.017
13 weeks	0.020	0.021
15 weeks	0.021	0.024
4 months	0.025	0.026
6 months	0.030	0.034

The sulfate resistance results, thus far, are very good for all the biomass samples. There is only one sample, 02-066, which has expansion values greater than the control mixture used for this procedural method. This, by the way, also is the same sample which failed the ASR expansion procedure. At the present time, all of the test samples have exhibited acceptable performance for expansion due to sulfate exposure.

Table 10. Length Expansion Results of Testing Biomass Samples for Sulfate Resistance

Test Age	Control	02-052	02-066	02-075	03-001	03-002	03-003
1 week	0.009	0.006	0.008	0.003	0.004	0.008	0.007
2 weeks	0.012	0.008	0.010	0.005	0.008	0.014	0.009
3 weeks	0.014	0.009	0.015	0.005	0.009	0.013	0.007
4 weeks	0.017	0.010	0.017	0.006	0.010	0.016	0.010
8 weeks	0.013	0.014	0.023	0.009	0.006	0.010	0.005
13 weeks							
15 weeks							
4 months							
6 months							

Zeolite Production

Recently, there has been a strong interest in cocombustion of biomass and coal fuels, partly to explore the use of renewable fuels and to relieve CO_2 emissions during coal combustion. The resultant biomass–coal fuel blend commonly has elevated alkaline-metal and alkaline-earth elements as compared to pulverized coal ash. The elevated alkaline content makes these ashes undesirable for use in many applications that have been identified as beneficial uses for fly ash. Therefore, most biomass–coal blend ashes are disposed of.

Zeolites are a beneficial mineral used for many applications in several different industries. They occur naturally in the southwestern United States where they are formed from the alteration of volcanic ash in alkaline-lake deposits. Zeolite synthesis can often be accomplished as less cost than long-distance transportation by adding alkaline compounds to CCBs and heating them at low temperatures in atmospheric pressures for relatively short periods of time (less than 48 hours). This work looked to exploit the alkaline content observed in those combustion ashes derived from cofiring biomass and coal blends. It is the high alkaline content, most notably Na and K, that make these ashes undesirable for use in most traditional CCB applications associated with the construction industry.

Mineralogy

Zeolites are a group of hydrated aluminosilicates of the alkali or alkaline-earth metals (primarily Na, K, Mg, and Ca). Zeolites have three-dimensional crystalline frameworks of tetrahedral silica or alumina anions strongly bonded at all corners. The zeolite structures contain (-Si-O-Al-) linkages that form surface pores of uniform diameter and enclose regular internal cavities and channels of discrete sizes and shapes, depending on the chemical composition and crystal structure of the specific zeolite involved. Pore sizes range from about 2 to 4.3 angstroms. The

enclosed cavities contain both the metal cations and water molecules. The cations are loosely bound to the lattice and can easily engage in ion exchange. The water molecules can also be reversibly driven off in most zeolites.

The pore sizes in zeolites allow them to function for gas adsorption, water adsorption/desorption, and ion exchange. Gas adsorption is the ability to selectively adsorb specific gas molecules. The ability of activated zeolites to adsorb many gases on a selective basis is in part determined by the size of the channels and according to zeolite type. Specific channel sizes enable zeolites to act as molecular gas sieves and can selectively adsorb various gases. Some zeolites have about 47% void space and a surface area of about 500 m^2/g. This means that this zeolite has a high rate of both sorption and ion exchange capacity. The ability of zeolites to adsorb certain gases makes them ideal for odor control applications. Zeolites are used in public toilets, horse stables, chicken coops, and feedlots, which all release ammonia fumes that can cause distress to both animals and humans.

Zeolites can have a high affinity for water and have the capability of adsorbing and desorbing water without damaging the crystal structure. This property makes them useful for desiccation and heat storage. Zeolites are used industrially to control moisture levels, particularly in low humidity ranges where other desiccants are less effective.

Synthetic zeolites

Zeolites have been produced from fly ash using a hydrothermal alkaline conversion.[1–5] Commonly NaOH or KOH solutions are used in atmospheric pressures at temperatures ranging from 80°C to 200°C and times ranging from 3 to 48 hours to prepare zeolites from fly ash. Kolay & Singh[4] made zeolites from ponded ash by adding KOH or NaOH at various concentrations and times. The temperature they used was 100°C. Querol and others[3] report an optimum temperature of 150°C for zeolite formation when activated by NaOH and KOH. There are about 40 naturally occurring zeolites, and more than 150 have been synthesized for specific properties such as adsorption, ion-exchange, molecular sieve, and catalytic properties.[5]

The largest use of synthetic zeolites has been as filler in powder detergents followed by catalytic applications for petroleum refinement. Applications as molecular sieves are minimal, and natural zeolites dominate that market.[5]

Experimental

Two ashes were selected based on their availability and chemistry for zeolite production. Both ashes were the result of full-scale cocombustion of coal and biomass. The chemical compositions as determined by x-ray fluorescence (XRF) are provided in Table 11.

Table 11. Chemical Composition of Full-Scale Biomass–Coal Ash, weight %

	CARCC 02-053	CARRC 02-0666
SiO_2	30.05	44.71
Al_2O_3	18.84	8.23
Fe_2O_3	1.28	3.8
CaO	19.83	28.01
MgO	8.27	2.59
Na_2O	0.36	2.9
K_2O	11.28	4.51
TiO_2	0.97	0.31
MnO_2	0.19	0.28
P_2O_5	2.16	1.26
SrO	0.43	0.14
BaO	0.28	0.31
SO_3	6.07	2.95

The samples selected were chosen because of their K_2O, Na_2O, and CaO content. These ashes were not suitable for application as a mineral admixture or cement replacement in concrete because of the alkaline content.

The first attempt to produce zeolites from these materials was a very simple approach in which 5 g of ash and 100 mL of water were heated to 90°C and stirred for approximately 48 hours. The ash was then removed, washed with distilled water, and submitted for x-ray diffraction (XRD) analysis. No zeolites were produced with this method.

Sample 02-066 was then placed in a Parr acid digestion bomb, which can be safely heated to 150°C. Three preparations were made, with the first being the ash as-received, the second with KOH added, and the third with NaOH added. For all three preparations, 1 g of ash was placed in the digestion bomb. 50 mL of distilled H_2O was added to one of the ash samples, and for the initial trial, a very strong alkaline solution was added as described by Querol and others.[3] The solutions were prepared as 3 molar solutions of KOH and NaOH in which 50 mL were placed into the digestion bomb with the 1g of ash. These were then placed in a Lindberg furnace for 48 hours and heated to 150°C. After heating, the samples were removed, filtered, and washed in distilled water. XRD analysis was performed on the three samples.

No zeolites were found by XRD analysis after 48 hours at 150°C. Figure 1 is the diffractogram of the ash and water with no additional alkali added. The original as received sample was found to contain lime (CaO) and calcite ($CaCO_3$) as minor constituents. After the heating process, the lime was absent and calcite was a major constituent. A calcium silicate phase also formed during the heating process.
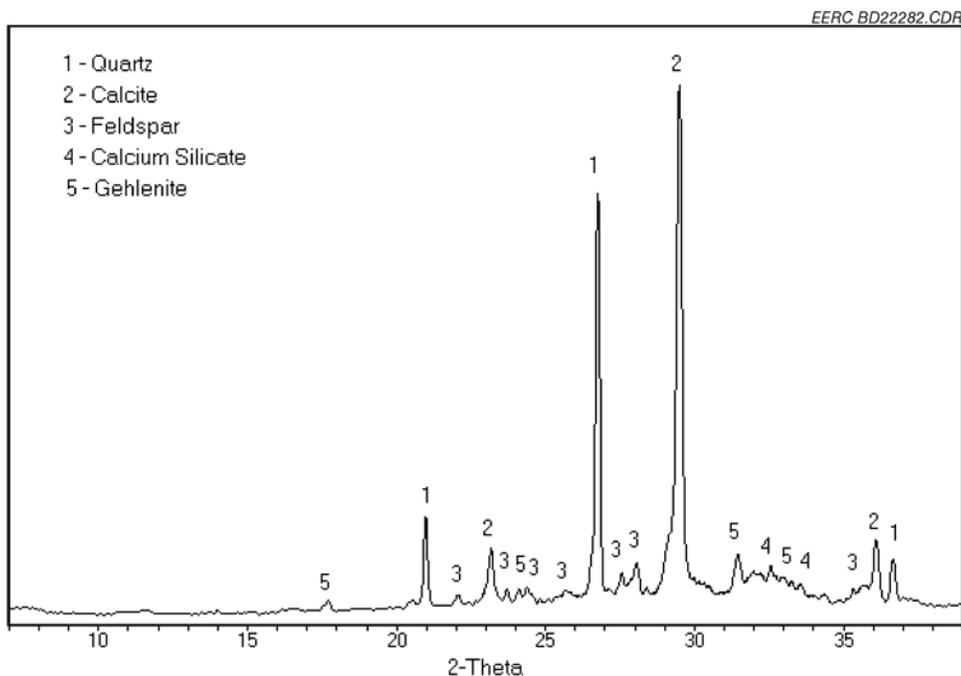
Figure 1. XRD diffractogram of Sample 02-066 after 48 hours of heating at 150°C.

Figure 2 shows the diffractogram of Sample 02-066 after 48 hour of heating at 150°C in the 3 molar solution of KOH. The primary difference in this sample was the formation of small amounts of portlandite $Ca(OH)_2$ and substantial amounts of tobermorite $Ca_5Si_6(OH)_{18} \cdot 5H_2O$. Portlandite may occur as an alteration product of calcium silicates in elevated pH conditions where the silicates are beginning to dissolve into the alkaline solutions. Tobermorite is known as a hydrothermal alteration product of calcium carbonate. It is often associated with zeolites, but it does not have the zeolite structure itself.

Figure 3 shows the diffractogram of Sample 02-066 after 48 hours of heating at 150°C in the 3 molar solution of NaOH. When compared to the diffractogram shown in Figure 1, the most noticeable difference is in the number of peaks present. Calcite is absent, and several different sodium carbonate phases were formed.

It appears as though the sodium was overwhelming to the experiment in that it replaced the Ca in the carbonates and formed several sodium carbonate phases. It is also likely that high-calcium ashes do not perform as well as low-calcium ashes in zeolite formation. The presence of the calcium silicates indicates that the high pH is causing silicon to go into solution, but it has a greater affinity for the calcium than the zeolites. A third attempt to form zeolites from CCBs was tried using CARRC Sample 02-053 and a low-calcium ash from the National Bureau of Standards, NBS 1633a, which was a standard reference material for trace elements with a known composition. While NBS 1633a is not an ash resulting from a coal and biomass blend of fuel, it was selected for its low Ca, Na, and K content to possibly better match the low-calcium ashes described as zeolite formers in the literature. Since the initial experiments failed to produce
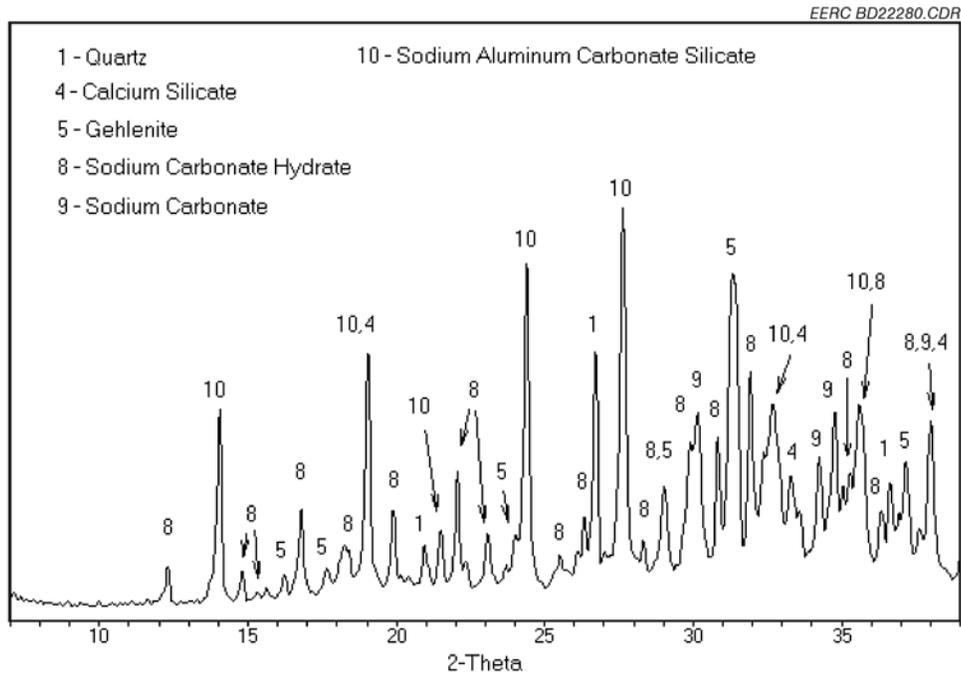
Figure 2. XRD diffractogram of Sample 02-066 after 48 hours of heating at 150°C in a 3 molar solution of KOH.
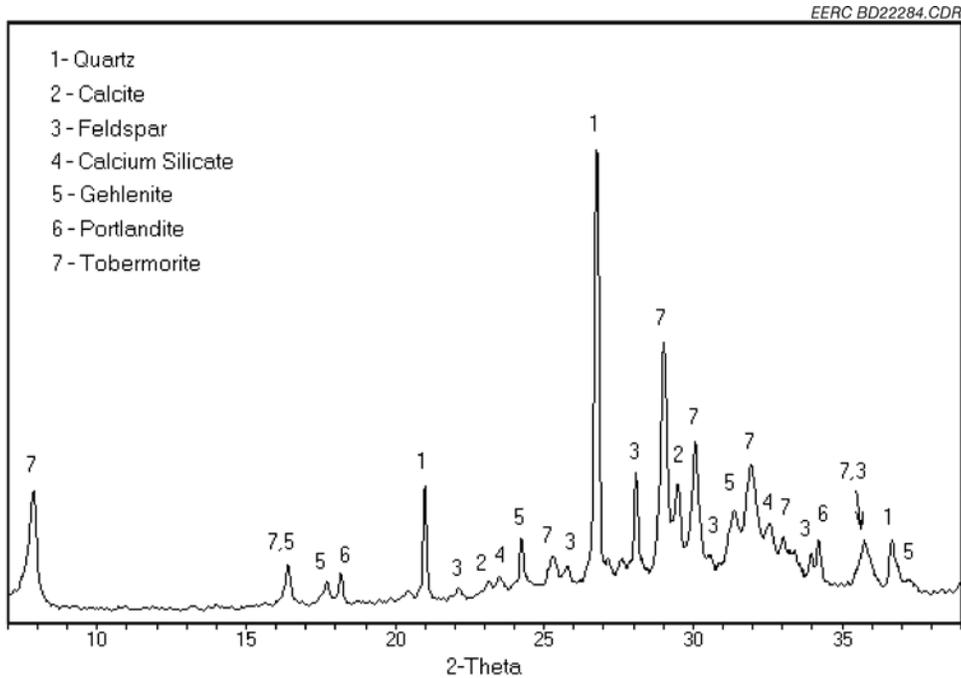

Figure 3. XRD diffractogram of Sample 02-066 after 48 hours of heating at 150°C in a 3 molar NaOH solution.

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zeolites, an ash with Si/Al ratios closer to those with known success was selected. A 1 molar solution of either KOH or NaOH was used rather than the 3 molar solutions previously. CARRC Sample 02-053 and a sample of NBS 1633a were activated with a 1 molar solution of KOH, and one NBS 1633a sample was activated with NaOH. All three samples were placed in a furnace heated to 175°C for 48 hours.

CARRC Sample 02-053 formed tobermorite and calcium silicate, but no other phases were found after the treatment. The NBS 1633a sample did form zeolites with both the NaOH and KOH solutions. Figure 4 shows the diffractogram of the NaOH added solution in which zeolite P1 formed. Zeolite P1 is a sodium-rich zeolite with the nominal composition of $Na_3Al_3Si_5O_{16} \cdot 6H_2O$. Tobermorite also formed, but no other zeolites. Figure 5 shows the diffractogram of the NBS 1633a sample with KOH added.

Figure 5 shows a diffractogram of NBS 1633a that was treated with a 1 molar solution of KOH at 175°C for 48 hours. As in the NaOH treated sample, zeolite P1 formed. Two other zeolite phases also were identified. Merlinoite and an unnamed potassium zeolite were identified. The nominal composition for merlinoite is $K_5Ca_2(Al_9Si_{23}O_{64}) \cdot 24H_2O$, and the unnamed zeolite phase has a nominal composition of $K_2Al_2O_4SiO_2 \cdot H_2O$. There is a large amorphous component not seen in the NaOH treated sample, and phases such as quartz, mullite, and anorthite were still identifiable in this sample and were essentially absent in the NaOH treated sample.

While the successful zeolite production was not done with a biomass and coal blended fuel ash, a low-calcium ash was not available. Future work in this area would involve finding such an ash
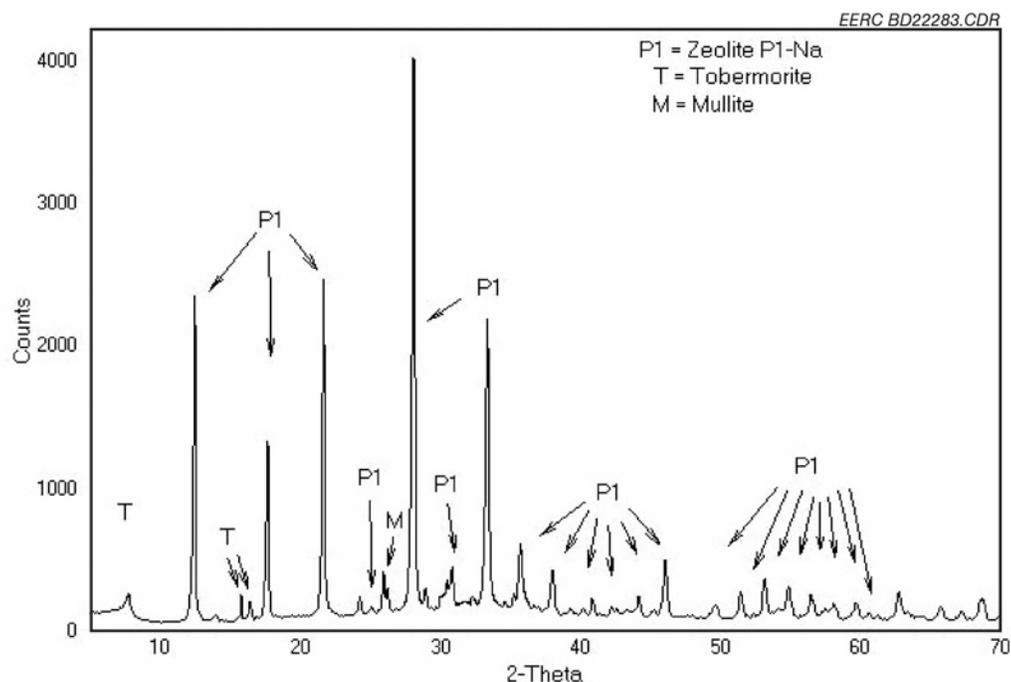

Figure 4. Diffractogram of NBS 1633a after 48 hours at 175°C in a 1 molar solution of NaOH.
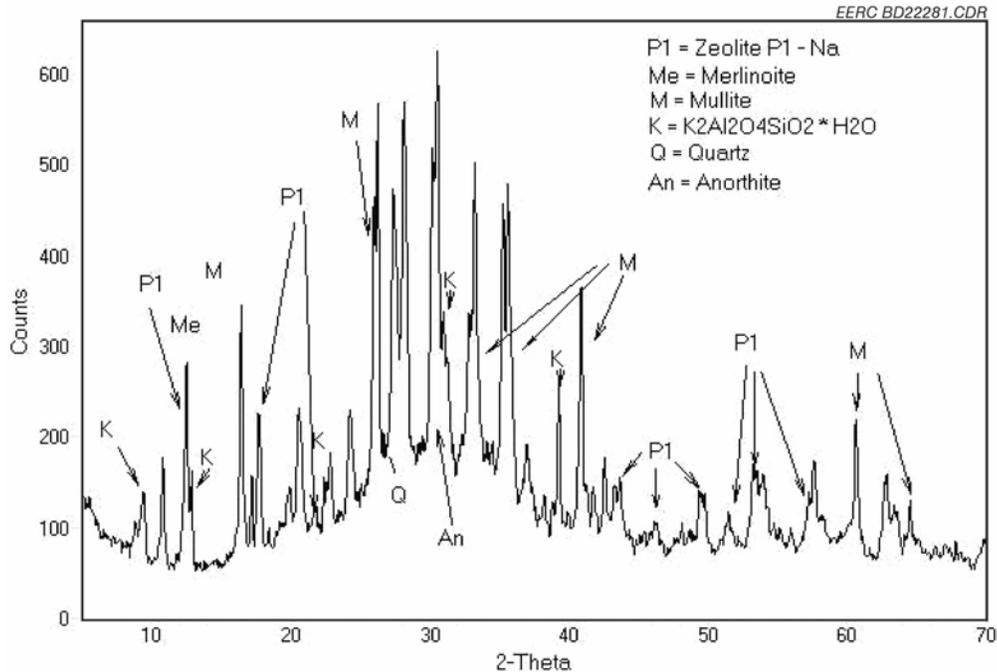
Figure 5. Diffractogram of NBS 1633a heated for 48 hours at 175°C in a KOH solution.

and determining time and temperature parameters for zeolite formation. Many zeolites contain Ca as a major component along with Si and Al. A well-defined experimental test matrix is necessary to determine the role Ca plays and how it can be exploited rather than be a hindrance. High-Ca ashes tend to be complex when compared to the low-Ca ashes or Class F ashes, which historically kept them from being considered as a resource. Zeolite production from high-Ca ashes is not reported in the literature. It is certainly easier to produce zeolites from low-Ca ashes than from high-Ca ashes but the techniques have not been properly investigated or reported for production from high-Ca ashes and biomass–coal ash blends.

Task 4 – Develop a Characterization Database

When the database development task was first initiated, small samples of coal–biomass fuel, coal samples, biomass samples, and ash from fuel and fuel blends were sought out and collected for input into the database. Once the majority of the sample data were collected, they were entered into tables of the database, either by the importing of already-electronic data or by data entry. The analysis on these samples collected include ASTM C618, computer-controlled scanning electron microscopy (CCSEM), Malvern, XRD, and XRF.

After data were collected and entered into tables in the database, relationships were established among tables to better query the data to obtain desired information. After proper querying was completed, forms and reports were generated to make the database more effective. The forms are used to enter in new data as well as for viewing and editing current data. Reports were generated for viewing purposes only.

At this point, a menu system was developed to create a sense of user-friendliness for the database users. The menu system gives the user the option to view a variety of forms and reports and to efficiently view, manipulate, and add data.

Once the work on the database itself was complete, a user's manual was developed. Composed of text and images of the database, it will assist users with navigation through the database and with questions they may have during navigation.

Task 5 – Reporting and Information Dissemination

The presentation at this conference is the first reporting and dissemination of these results.

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