The Utilization Potential of Anthracite CFBC Spent Bed Fly Ash as a Concrete Additive.

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Abstract

Fluidized bed combustion's remarkable ability to use high ash fuels has resulted in its use to recover power from anthracite coal refuse. The spent bed material produced differs from that of high sulfur bituminous coal, having a much lower calcium sulfate content (~6% vs. ~20%). This is an artifact of both the high ash and lower sulfur of the anthracite fuel. The remainder of this material consists of devitrified clay materials, quartz and lime. Fly ash from the anthracite refuse was investigated for use as a pozzolanic admixture to Portland cement. The material was dry milled to an average particle size (D_{50}) of about 8 μm and tested for mortar strength and expansion. Unlike conventional pulverized coal combustion fly ash, this material is not rounded or vitrified. Its irregular shape and higher surface area results in higher water demand, but this is compensated to some extent by higher surface area and reactivity. Strength index measurements (SI) greatly exceeded the minimum criteria as set for by ASTM C-618 for a Class F ash, achieving strength index values as high as 130% of control at 56 days. Expansion tests indicated that this FBC material will not present dimensional stability problems. Overall, the use of this material as a pozzolanic additive appears promising.

Introduction

Fluidized bed combustion's remarkable ability to use high ash fuels has resulted in its use to recover power from both bituminous and anthracite coal refuse. The fly ash used in this study was obtained from an Anthracite waste fueled cogeneration plant. The plant is rated at 98 megawatts and employs circulating fluidized bed boiler technology with limestone injection. The annual fuel consumption is approximately 545,000 tons, and primarily consists of fine and coarse refuse left over from legacy mining operations. The amount of ash generated annually is approximately 400,000 tons, of which 85 percent is fly ash and 15 percent is bottom ash.

The physical and chemical characteristics greatly differ in ash produced from a bituminous fluidized bed combustion boiler. The high ash content of this fuel reduces the retention time of the fuel in the combustor for any given heat load. This results in a relatively diluted calcium sulfate and residual lime content of the spent bed material. This is illustrated in Table 1 which compares the chemistry of this material to that from the fluidized bed combustion of high sulfur coal and more conventional PCC Class F and Class C fly ash. The spent bed material from the anthracite refuse differs from that of high sulfur bituminous coal, having a much lower calcium sulfate content (~6% vs. ~20%). This is an artifact of both the high ash and lower sulfur content of the anthracite fuel.

The relative degree of sulfation of the calcium is similar between the two different fluid bed materials studied. It was shown that 27% of CaO was tied up as sulfate in the anthracite fly ash, and 33% was tied up in the bituminous material which was studied previously [1]. The remainder of this material consists of devitrified clay materials, quartz and lime.

Ash from fluidized bed combustion generally has not been used as an additive in Portland cement concrete. Much of it falls outside the range of composition as set forth in ASTM C-618 [2] which limits sulfate content to 5.0% as SO_3. It is also not glassy like fly ash that is produced by pulverized coal combustion.

Research Strategy

The lower operational temperature of fluidized bed combustors is below the melting point of the constituents of the ash. The solids produced are not glassy, and the clay minerals are calcined to the point of being non crystalline to X-ray diffraction. They are more similar to metakaolin, a calcined clay, than glassy PCC ash. Metakaolin is a highly reactive and valuable pozzolanic additive for concrete. It is highly reactive, and because of its size, it has a great filler effect in the concrete. The clay minerals in coal refuse, with some notable exceptions, are predominately illite and chlorite. Kaolinite is a 1:1 clay that is one layer of tetrahedrally coordinated silica to one layer of octahedrally coordinated alumina. The clay minerals in coal refuse are 1:2 layer clays; that is, one octahedral alumina layer sandwiched between two tetrahedral layers of silica. These sandwiches are then bonded together either with a potassium layer, in the case of illite, or a brucite (MgO) layer in the case of chlorite [3,4].

Because of the similarities, we prepared the anthracite refuse fly ash (referred to as AR-FA herein) by first dry milling it to achieve a smaller particle size, similar to that of metakaolin. We found that the anthracite refuse material could be dry-milled without much difficulty. This was not the case with the FBC fly ash, which had been investigated previously. The FBC fly ash tended to cake up in the mill, most likely due to its higher content of anhydrite.

Materials Preparation and Testing

The AR-FA was dry milled in batches of 1 kg in a small laboratory ball mill for 1 hour. An average particle size (D_{50}) of approximately 8-9 μm was achieved. It was determined that milling times much longer than this did not produce substantially finer material.

The AR-FA was analyzed chemically by X-ray fluorescence, using appropriate mineral and rock standards for calibration. This data, which was produced by the fluidized bed combustion of high sulfur bituminous coal, along with the analysis of a typical Class F and Class C fly ash, can be found in Table 1.

The pozzolanic activity of the material was determined using standard ASTM mortar test procedures [5,6,7]. The AF-FA was premixed at a substitution rate of 20% with ordinary Portland cement (OPC), obtained at a local building supply center. The 500 grams of the cementitous material, along with 1375 g of standard graded Ottawa sand and 242 g of water, were used to form 2 inch (~50 mm) test cubes for the control. The AF-FA test mixes were adjusted to have similar flow to the control by addition of water. A total of 250 g of water (103%) was needed to duplicate the flow of the control. A second test was made by adding a small amount (~1 g) of a commercial high range polycarboxylate based water reducer (BASF GLENIUM® 3030 NS). The cubes were demolded after 24 hours and were tested in duplicate.

Table 1. Comparison of composition of FBC materials

	FBC-AR FB	FBC-Hi Sulfur Bituminous	PCC-F	PCC-C
Major elements				
SiO_2	56.00	26.05	49.75	32.30
Al_2O_3	21.24	10.59	24.76	18.10
Fe_2O_3	6.14	10.06	12.22	6.50
CaO	8.61	29.76	4.31	26.40
MgO	1.20	3.64	1.36	5.80
Na_2O	0.29	0.17	0.48	2.40
K_2O	2.63	1.36	2.24	0.33
P_2O_5	0.1	0.1	0.32	1.00
TiO_2	1.35	0.45	1.18	1.40
SO_3	3.6	15.42	0.48	
%C		4.93	4.07	
LOI		9.13		
Trace elements				
V	253	<1	250	
Cr	98	29	70	62
Mn	202	117	165	200
Co	19	21	41	28
Ni	70	19	66	32
Cu	108	<1	225	
Zn	2227	<1	135	
As	40	83	153	18
Rb	10	123	24	
Sr	540	206	1072	
Zr	8	20	310	
Mo	106	<1	24	
Cd	1	1	4	1
Sb	3	7	2	3
Pb	49	33	72	38

A second set of tests were conducted to compare the milled anthracite refuse with metakaolin. A commercially available metakaolin (BASF MetaMax®) was used in the tests. The mean particle size of the metakaolin was approximately 4 µm, as determined by laser diffraction particle size analysis, compared to ~8 µm for the AR-FA. The overall surface area, as determined by BET nitrogen adsorption, was higher for the AR-FA; 15.13 m^2/g versus 9.46 m^2/g for the metakaolin. OPC substitutions of 10% and 20% for both the metakaolin and the AR-FA were made. The flow of the mortar pastes were measured on a flow table and the water was adjusted to make the flow consistent with the control. The second OPC (OPC II) was different for this set of tests, having run out of the previous cement used in the first part of the study. The second cement was markedly different than the first. It provided considerably stronger mortar cubes compared to the first cement, and its flow also differed being slightly more viscous. (Figure 1). This was an unanticipated, and very much undesired, additional variable in the study.

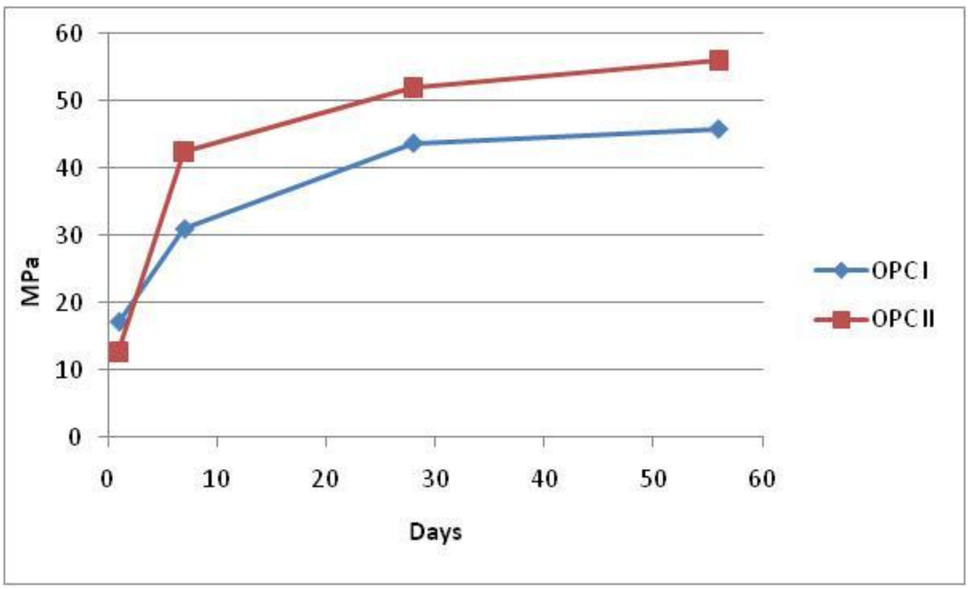

Figure 1. Plot of mortar strength development for the two OPCs used in the study.

Additionally, to test the dimensional stability of the AR-FA, expansion tests were run in accordance with ASTM procedures [8,9]. In these tests, 1 inch square (~25mm) bars, 10 inches (25.4 cm) in gauge length, were cast and cured in a misting chamber at 100% relative humidity. The change in length of the bars is measured over time and the changes are recorded as percent lengthening or shortening.

Test Results

The mortar strength results are plotted in Figure 2. Unlike conventional pulverized coal combustion fly ash, this material is not rounded or vitrified. Its irregular shape and higher surface area resulted in higher water demand (103% of control), but this is compensated for by higher surface area and high reactivity. Strength index measurements (SI) at 7 and 28 days were found to equal or exceed that of Portland control and reached a value of 130% at 56 days. Expansion tests indicated that this FBC material will not present dimensional stability problems. Overall, the use of this material as a pozzolanic additive appears promising.

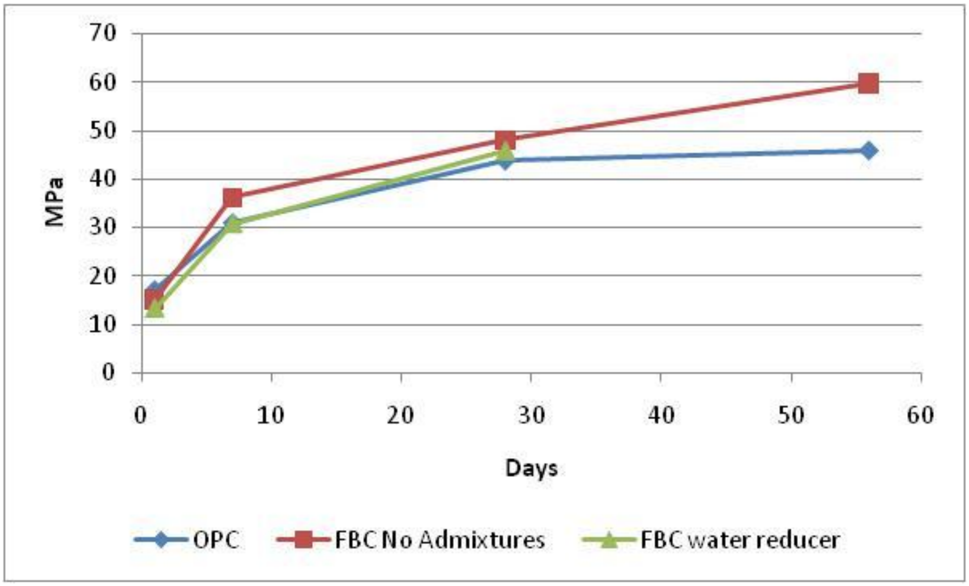

Figure 2. Mortar strength data for AR-FA with OPC I.

The mortar strength comparison with the metakaolin and the AR-FA is presented in Figure 3. The work was performed with the second Portland cement, OPC II. The samples were prepared with constant flow and had a wide range of water demand. For example, the metakaolin required 102% of the control at 10%, but at 20% substitution the mortar became sticky and required 118% of the control water (287 g versus 242 g). The AR-FA required 103% at 10% substitution and 106% at 20%. It is noted here that in the tests with the OPC I, the water demand only increased 3% over that of control at 20% substitution. The additional water required by these materials resulted in decreased strength for the higher substitution levels. Regardless, all of the materials tested passed the strength requirements of ASTM C-618 standard.

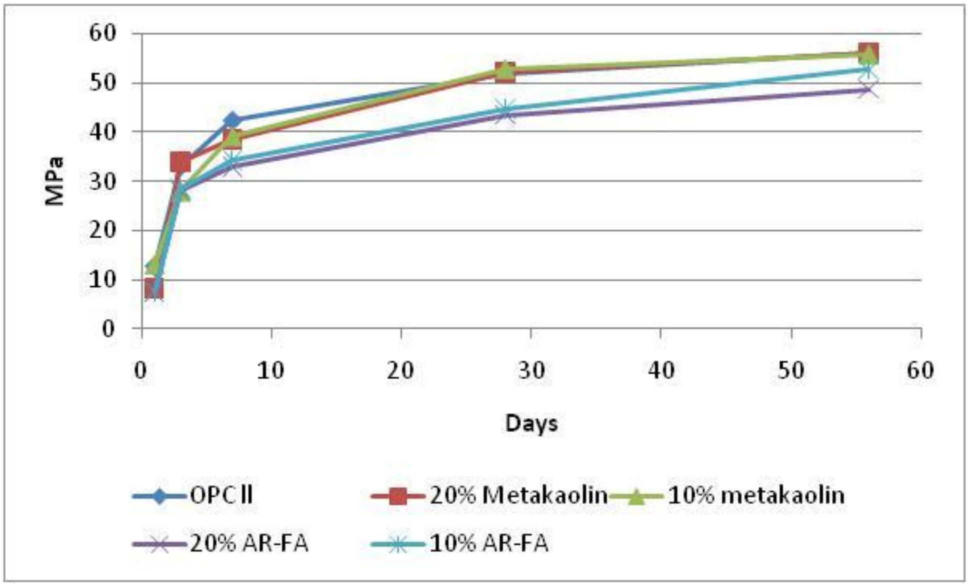

Figure 3. Mortar strength data for AR-FA and metakaolin with OPC ll.

The results of the dimensional stability of the AR-FA were very good. Changes in the length of the bars were relatively small. For example, the average expansion of the control OPC I was 0.031%. The average AR-FA was measured as 0.034%, and the AR-FA with the water reducer was -0.068 at 4 weeks. Measurements at 8, 16, 32 and 64 weeks found no additional changes in dimension beyond the range of measurement uncertainty. Also, the bars did not show any obvious deterioration or cracking over the period of testing.

Conclusions

The study clearly indicated that the anthracite refuse fly ash had pozzolanic activity and would meet the ASTM C-618 for a Class F pozzolan. Unlike most other fluidized bed products, the AR-FA would meet all of the requirements of a Class F fly ash, having an SO_3 content below the 5.0% upper limit. The expansion tests also indicated that the AR-FA would have good, and perhaps exceptional, dimensional stability.

The AR-FA was found to have variable strength benefit, providing increased strength when used with lower performing cement (the OPC I). These increased strength index values reached levels of 130% of control at 56 days. When used with higher performing cement, it did not provide a benefit of increased strength with most samples in the 90% to 100% range at 28 and 56 days. The reason for this is unclear; however, we have observed this before with other kinds of pozzolans including Class F and Class C fly ash from PCC boilers. This may be due to particle size, or major component differences, particularly in the content of tricalcium aluminate and alite, or alkalinity differences in the OPC's.

Future Test Works

The results of our investigation to date have demonstrated that the anthracite refuse fly ash has good pozzolanic activity. It can be used to replace Portland cement and produce mortars of equivalent, or even enhanced, strength and good dimensional stability. The next step in the investigation is to determine the impact on the overall durability of OPC concrete and its effect on air entrainment and workability.

References

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