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Commercial Demonstration of High-Carbon Fly Ash Technology in Cement Manufacturing

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ABSTRACT

A large-scale demonstration using high-carbon fly ash as cement raw feed component was carried out at Illinois Cement. The demonstration used large volume of high-carbon fly ash from Ameren's Coffeen Power Station in Illinois. Nearly 200 tons of the fly ash was used at a rate of 3.5% addition to the cement plant raw mix and ran for nearly three days.

Use of high-carbon fly ash at the cement plant realized several material, product and environmental benefits. These included a reduction of fuel consumption, increase in clinker production, and reduction in NO_x emissions. A significant improvement in cement quality its compressive strength was also evidenced. Cement produced during the demonstration exhibited physical properties far exceeding the required standard specifications.

This successful demonstration points to the emergence of a viable large-volume market for high-carbon fly ash that offers several material, operational, and environmental benefits to both electric power generation and cement industries.

KEYWORDS: Fly ash, high-carbon fly ash, cement manufacturing, raw materials, cement raw feed component, fuel supplement, cement testing, clinker evaluation

INTRODUCTION AND BACKGROUND

Over 3 million tons of fly ash is annually generated in Illinois; less than two-third of which is used in commercial products. The rest is landfilled. The continued implementation of the environmental polices to reduce NO_x emissions at coal-fired power plants will further increase the production of fly ash with significant contents of unburned carbon.

The high-carbon fly ash cannot be used in most concrete, as the carbon content can greatly decrees the durability and performance of concrete. The goal of this project was to determine if the high-carbon fly ash could be used in the manufacture of cement which is a critical component of concrete.

In typical cement manufacturing, silica, alumina, and iron contents are necessary ingredients in cement raw mix. Since fly ash is typically rich in these compounds, it can be conveniently used in cement raw feed, whereas the unburned carbon in fly ash functions as a fuel supplement in the energy intensive cement manufacturing process.

This paper presents an account of large-scale demonstration that involved a cement plant and fly ash producer operating in Illinois. They are respectively, Illinois Cement and Ameren's Coffeen Power Station. During the commercial-scale demonstration, large volume of high-carbon fly ash from the power station were utilized. The fly ash was blended with the cement plant's raw mix, converted into cement clinker, and then ground into portland cement. Cement and clinker samples were tested, evaluated, and compared to those normally produced at the plants. During the demonstration, the performance of the manufacturing process along with the material, and production benefits resulting from the use of high-carbon fly ash were documented.

Material Characterization

Prior to the demonstration, the fly ash was analyzed for its composition and compatibility with cement raw mix. The composition of the ash is shown In Table 1; which also shows nearly 13% loss of ignition (L.O.I.) that can largely be attributed to the unburned carbon.

Table 1. Oxide composition of Coffeen fly ash

Analyte	Wt., %
SiO_2	47.87
Al_2O_3	17.08
Fe_2O_3	8.59
CaO	4.68
MgO	1.21
SO_3	0.21
Na_2O	2.02
K_2O	2.77
TiO_2	1.13
P_2O_5	0.23
Mn_2O_3	0.04
Loss on Ignition (L.O.I)	12.97

The fly ash was also tested by differential scanning calorimetry (DSC) to determine its fuel content and the presence of any organic volatile species, which can cause emission-related issues. The DSC plot for the fly ash is shown in Figure 1. A large exothermic peak at temperatures above 450°C confirms the presence of substantial heat content in the fly ash, whereas, a lack of any exothermic peak at temperatures below 450°C suggests an absence of volatile matter in the fly ash.

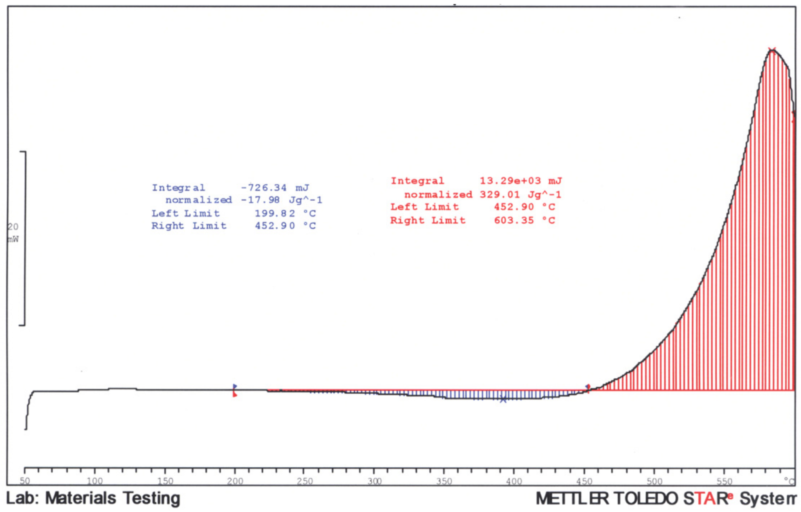


Figure 1. DSC Plot of Coffeen Fly Ash Sample

Also of interest in the plot is the presence of endothermic hump (negative hump) below 450°C. This heat consuming property of the fly ash tends to contribute to a reduction of temperature in the upper portion of the preheaters at cement plants leading to clearer pathways and smoother material flow of the feed load.

Raw Mix Formulation

The material analyses of the fly ash and of the cement kiln feeds without and with the anticipated fly ash addition (3% by wt.) prior to the demonstration is shown below in Table 1. The purpose of the run was to determine benefits in production rate, fuel usage, operations continuity, and product quality that might be achieved as a result of the inclusion of high-carbon fly ash. The impact on environmental emissions was also to be evaluated.

Table 1. Composition of kiln feed with and without the high-carbon fly ash

Analyte	Kiln feed	Kiln feed + 3% fly ash
SiO_2	19.50	22.37
Al_2O_3	5.40	6.64
Fe_2O_3	2.32	2.84
CaO	66.67	61.90
MgO	3.25	3.06
SO_3	0.94	0.91
Na_2O	0.30	0.44
K_2O	1.04	1.30
TiO_2	0.28	0.37
Mn_2O_3	0.21	0.20
Loss on Ignition (L.O.I)	0.00	0.00

DEMONSTRATION AT ILLINOIS CEMENT

The demonstration was carried out at Illinois Cement which is a dry processing plant with multistage cyclone preheaters (Figure 2). Nearly 200 tons of high-carbon fly ash from the Coffeen Power Station was pneumatically trucked and blended at a 3.5% addition rate with the raw mix at Illinois Cement. The demonstration ran for nearly three days.

Figure 2. The Illinois Cement plant with clinker a capacity of 1700 t/day

Clinker Characterization

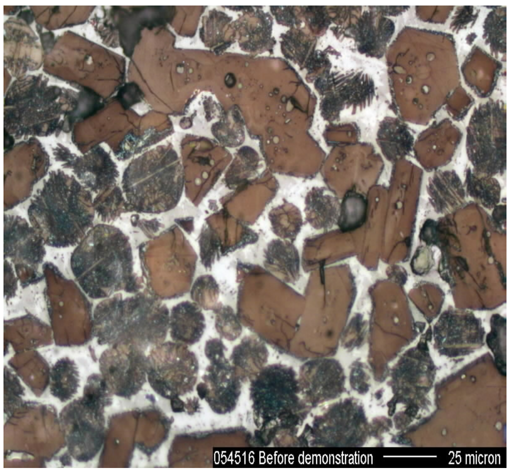
The clinkers produced before and during the demonstration were collected and tested for oxide analyses and Bogue composition (Table 2a,b). The corresponding photomicrographs of these clinkers are shown in Figure 3.

Table 2a. Clinker composition (wt. %) before and during demonstration

Analyte	Before	During
SiO_2	21.04	21.06
Al_2O_3	5.89	5.90
Fe_2O_3	2.46	2.55
CaO	63.79	63.32
MgO	2.42	2.92
SO_3	1.95	1.79
Na_2O	0.45	0.46
K_2O	1.19	1.19
TiO_2	0.33	0.33
P_2O_5	0.13	0.12
Mn_2O_3	0.22	0.22
Loss on Ignition (L.O.I)	0.22	0.18

Table 2b. Bogue composition of clinkers before and during demonstration

Calculated Bogue Compounds, wt. %		
Phase	**Before**	**During**
C_3S	51	49
C_2S	22	23
C_3A	11	11
C_4AF	7	8

a) 

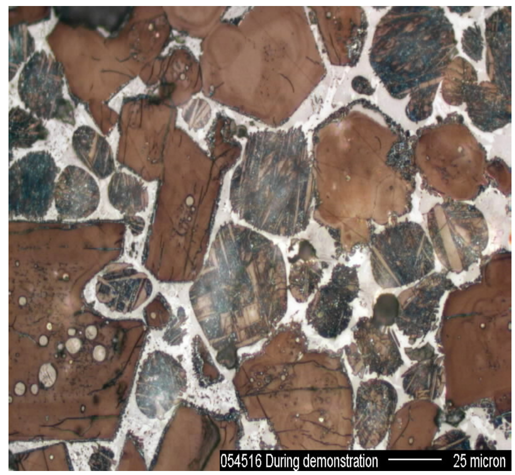
b) 

Figure 3. Photomicrographs of a) clinker before demonstration (without fly ash), and b) clinker produced during demonstration (with fly ash).

The large angular crystals in the micrographs (Figure 3a,b) are alites (C_3S), and the round crystals with lamellae are belites (C_2S). The interstices are composed of tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), also known as the melt phases.

As can be seen in clinkers produced before the demonstration (Figure 3a), alite crystals are large and cannibalistic (crystals are "glued" together along exterior edges). Alite crystals also show relatively shallow etch and indicate sluggish hydraulic activity. Belite crystals are moderate in size, with ragged edges indicative of slow cooling. Some belite crystals are internally disintegrated. Such crystals would not be expected to contribute to cement strength development. Aluminate and ferrite crystals are coarsely crystalline, suggesting slow cooling. Porosity appears to be very low.

In clinker made during the demonstration (Figure 3b), the alite crystals are large, and cannibalism appears somewhat less apparent than from sample before burn. Alite etch appears deeper by virtue of improved color contrast and can therefore contribute to better strength. The belite crystals are moderate in size and their edges are ragged, but cooling appears to be a little faster than for the previous sample. The aluminate and ferrite crystals are coarsely crystalline, and porosity is very low.

Cement Production and Evaluation
The clinker produced during demonstration was ground with appropriate amount of gypsum to produce cement for testing and evaluation in accordance with the ASTM C 150 specification. The results are shown in Table 3. Data on cements produced before and after the demonstration are also shown for comparison.

Table 3. ASTM C 150 data of cements produced

	Before	**During**	**After**	**ASTM limits**
ASTM C 204 - Fineness, air permeability (Blaine), m^2/kg				
	375	372	382	280 (min)
ASTM C 109 - Compressive strength, psi				
3-day	3130	3490	2910	1740 (min)
7-day	4070	4250	3940	2470 (min)
28-day	5020	5290	5050	4060
ASTM C 191 – Vicat time of set, minutes				
Initial	135	120	110	45 (min)
Final	160	140	130	375 (max)
ASTM C 185 – Air content, %				
	7.2	7.1	5.9	12 (max)
ASTM C 151 – Autoclave expansion, %				
	-0.34	0.11	0.16	0.80 (max)

It is evident from the data that the cement produced during demonstration complied with all requirements established by ASTM Specification C 150. However, the demonstration cement had the best strength performance of all the other cements at all ages, despite a slightly lower fineness. The time of set, air contents, and autoclave results were normal for the demonstration cement.

Stack Emissions
To assess the effect(s) of the use of high-carbon fly ash on the operation, the stack was monitored for emissions of oxides of nitrogen (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO), and for content of carbon dioxide (CO_2), oxygen (O_2), and water vapor (H_2O). In addition, the total gas flow, temperature, and pressure were recorded. The results are summarized in Table 4.

It can be seen from the data that the emissions of NO_x were lower for the time period during which the fly ash was included in the mix. CO emissions were higher during and after the fly ash burn than before the burn. SO_2 emissions, which were very low throughout, were not changed significantly.

Table 4. Data on stack emissions before, during, and after demonstration

Emissions	Before	During	After
NO			
lb/hr	209	200	273
lb/ton clinker	2.65	2.53	3.56
CO			
lb/hr	95.3	276	158
lb/ton clinker	1.21	3.60	1.99
CO_2, %	15.2	16.6	16
H_2O, %	9.1	9.1	9.2
SO_2, ppm	11.6	47.0	25.8
O_2, % dry	11.7	11.2	11.2
Flow, Wet SCFM	156092	156092	156092

Critical Operational Observations
Other critical operational observations documented during demonstration can be summarized as follows:
1) Fly ash being free flowing material was handled pneumatically and blended easily without any grinding pre-processing
2) Operation ran predictable, smooth, and normal. No undue effects to operation were caused by the incorporation of high-carbon fly ash in the raw mix.
3) Fuel consumption during the observation reduced by 2.6% due largely to the presence of unburned carbon in the fly ash.
4) Clinker production was noted to have increased.

From the operational as well as material standpoints, the demonstration on the use of high-carbon fly ash in cement manufacturing was successful.

CONCLUDING REMARKS

The commercial-scale run clearly demonstrates that cement manufacturing can be employed as a large volume consumer of high-carbon fly ash. The demonstration points to the emergence of a market for the otherwise non-usable high-carbon fly ashes with tangible material, operational, product, and environmental benefits to both the electric power generating and cement industries.

ACKNOWLEDGEMENTS

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