Operational Benefits of Using High-Carbon Fly Ash in Cement Manufacture

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ABSTRACT

More than half of the total fly ash produced in the US is landfilled because its carbon content is too high for use in concrete. High carbon content in fly ash is either due to compliance with the emission regulations or operating older and less efficient plants. By virtue of its compositional similarity to shale/clay, high-carbon fly ash has been used in cement raw feed and has imparted many operational benefits. Several commercial demonstrations were carried out in which nearly 1000 tons of fly ash with up to 20% carbon replaced up to 6% of cement plant raw mix. This paper discusses selected demonstrations in which high-carbon fly ash from a Midwest station was used in a preheater process cement plant. Because of the additional heat derived from carbon, the use of fly ash essentially transformed the preheater process into a semi-precalciner process. During the demonstration several key operational parameters were improved; the kiln operation ran efficiently and smoothly; the plant realized a fuel savings of nearly 4% and a 10% increase in production. The resulting cement met the ASTM C 150 requirements. With this approach, large-scale reutilization of discarded fly ash is possible.

1. INTRODUCTION AND BACKGROUND

Coal-fired power stations in the United States generate nearly 72 million tons of fly ash [1]. Nearly 40% of the fly ash is used in commercial products and the remainder is discarded. The implementation of any future clean air regulation at coal-fired power stations will very likely increase the production of fly ash with significantly higher unburned carbon contents. Cement plants are routinely seeking alternatives to their natural raw materials and fossil fuels, and fly ash being rich in silica, alumina, and iron – which are necessary components of the cement raw feed – presents a convenient choice as a raw feed component in cement manufacturing [2]. The fly ash would partially replace raw materials such as shale or clay; whereas carbon will serve as a fuel supplement during the cement manufacturing process [3].

To demonstrate this concept, nearly 100 tons of high-carbon fly ash from a Midwest coal-fired power station was used in the raw mix of a cement plant also located in the Midwest. During the demonstration, several material and operational benefits were realized which are discussed in this paper. This approach offers a large-volume use of otherwise unusable high carbon fly ash, and if implemented, can reduce >10% of all wasted fly ash in the US.

2. DEMONSTRATION PARTICIPANTS

2.1 Coal-Fired Power Station in the Midwest

The power station that participated in the demonstration is located in the Midwest (Fig. 1). This power station annually produces 80,000 tons of dry fly ash that contained ≈20% unburned carbon at the time of the demonstration.

Figure 1. Coal-Fired Power Station and Cement Plant in the Midwest

2.2 Cement Plant in the Midwest

The participating cement plant is also located the Midwest (Fig. 1). The cement plant is a dry process operating with four-stage preheater kiln system and normally produces ASTM C 150 Type I Portland cement. The plant has a production capacity of 1,400 tons clinker/day, and uses coke and natural gas as the primary fuels. The principal raw materials used in the plant, i.e., limestone and shale, are quarried and transported from a nearby location.

3. MATERIALS CHARACTERIZATION

Prior to the demonstration, both the cement raw feed and fly ash were analyzed to determine their compatibility for optimum use in the raw mix.

3.1 Cement Plant Raw Feed

Raw feed used at the cement plant prior to demonstration was analyzed and is shown as the target raw feed in Table 1.

Table 1. Target Composition of Cement Raw Feed

Oxide Analysis	Weight, %
SiO_2	13.74
Al_2O_3	3.91
Fe_2O_3	1.76
CaO	41.79
MgO	1.64
SO_3	0.57
Na_2O	0.32
K_2O	0.75
Loss on Ignition (L.O.I.)	35.08
Total	100.09

3.2 Power Station Fly Ash

Two fly ashes (Samples A and B) were collected from the power station and characterized for their chemical and mineralogical compositions, heat content, and particle size distribution.

3.2.1 Chemical Composition: The oxide analysis of the fly ash (Samples A and B) are presented in Table 2. Their losses on ignition (L.O.I.) are 20.83% and 12.97% respectively. The L.O.I. is attributed to the presence of high unburned-carbon of the ash.

Table 2. Oxide Composition of Fly Ashes, wt. %

Oxide Analysis	Sample A			Sample B
	Truck 1	Truck 2	Composite	Composite
SiO_2	42.38	43.51	42.95	47.87
Al_2O_3	15.13	15.79	15.46	17.08
Fe_2O_3	6.75	7.45	7.10	8.59
CaO	4.45	4.49	4.47	4.68
MgO	1.26	1.33	1.30	1.21
SO_3	0.49	0.48	0.49	0.21
Na_2O	1.80	1.96	1.88	2.02
K_2O	2.43	2.57	2.50	2.77
L.O.I.	22.20	19.45	20.83	12.97
Total	98.30	98.53	98.42	99.01

3.2.2 Mineralogical Characterization: Typical XRD patterns of fly ash Sample A (Truck 1 and 2), in Fig. 2, indicate the presence of quartz, magnetite, calcium aluminate, calcium silicate, lime, and anhydrite. Of interest is the “hump” peaking at 25-2θ angle confirming the glassy content, which renders the fly ash reactive to lime at elevated temperatures.

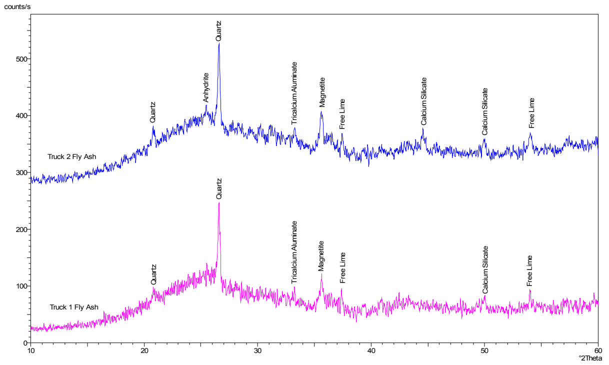


Figure 2. Typical XRD Patterns of Fly Ash (Angle 2θ is from 10 to 60°)

3.2.3 Heat Content: Differential Scanning Calorimetry (DSC) was used to test the fly ashes for their fuel values and also for the presence of volatiles *vis a vis* their temperatures of release. A typical DSC plot for one of the Sample A ash is shown in Fig. 3.

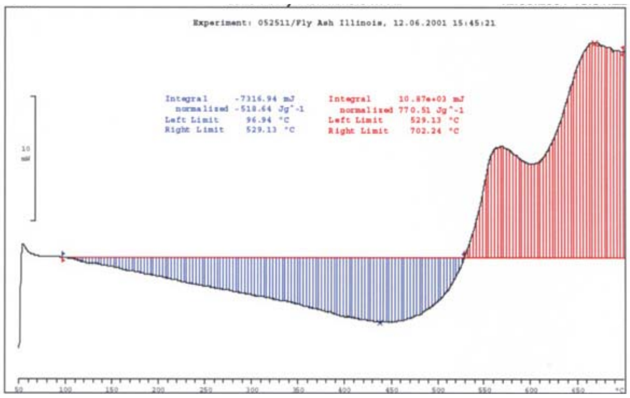


Figure 3. DSC Result from Fly Ash Sample A Composite

The large exothermic peak at temperatures above 550°C (1020°F) indicates the presence of substantial heat content in the ash. From the DSC data, the average total heat content (calorific value) of the ash was estimated to be greater than 318 Btu/lb (178 kcal/kg). Assuming that the fly ash is utilized at a rate of 6% of the kiln feed, the anticipated energy contribution from the fly ash is 57,300 Btu (14,440 kcal) per ton of clinker. The lack of any exothermic peaks at temperatures less than 550°C (1020°F) confirms the absence of organic emissions at lower temperature [4]. This suggests that very little volatile matter will be released from the ash. In fact, the endothermic peak below 550°C (1020°F) suggests a heat-absorbing property of the ash which might prevent overheating of raw feed in the initial stages of preheaters [5,6].

3.2.4 Particle Size Distribution. Particle size distributions of fly ash A composite is shown in Fig. 4. As expected, the fly ash was a particulate and finely divided material. The average size was less than 325-mesh (45 μm).

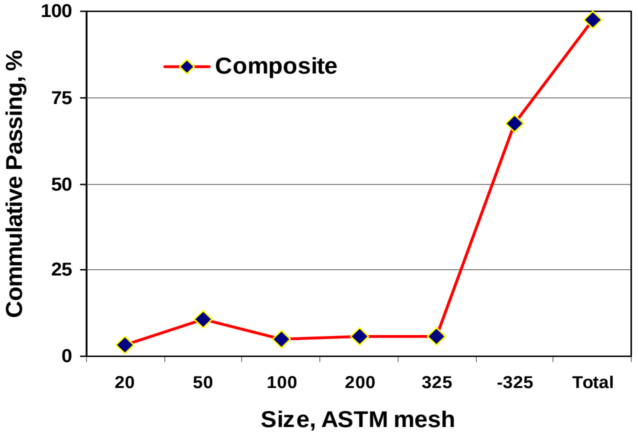


Figure 4. Particle Size Distribution of Fly Ash Sample A Composite

3.3 Compatibility of Fly Ash with Cement Raw Feed

Since the fly ash was primarily intended to replace shale in cement raw mix, its chemical composition was compared with that of the shale. As seen from the data in Table 3, the composition of the fly ashes on ignited basis appears similar to that of shale. Furthermore, both the physical properties (dry, particulate, fine size distribution, and free-flowing material) and the mineralogical properties (presence of amorphous glassy content) render the fly ash a convenient replacement for shale in the cement raw mix.

Table 3. Fly Ashes and Shale Composition on As-Received and Ignited Basis

Oxide Analysis	As-Received Basis, %			Ignited Basis, %		
	Fly Ash A Composite	Fly Ash B	Shale	Fly Ash A Composite	Fly Ash B	Shale
SiO_2	42.95	47.87	54.3	57.5	55.58	60.4
Al_2O_3	15.45	17.08	17.5	20.7	19.83	19.5
Fe_2O_3	7.1	8..59	8.6	9.51	9.97	9.57
CaO	4.47	4.68	8.6	5.98	5.43	4.23
MgO	1.3	1.21	2.3	1.74	1.41	2.56
SO_3	0.49	0.21	0.3	0.66	0.24	0.33
Na_2O	1.88	2.02	0.7	2.52	2.35	0.78
K_2O	2.5	2.77	2.4	3.35	3.22	2.67
L.O.I.	20.83	12.97	8.1	–	–	–

4. COMMERCIAL SCALE DEMONSTRATION

Nearly 100 tons of high-carbon fly ash was collected from the power station and transported to the cement plant using pneumatic trucks. Prior to the demonstration, the fly ash was blended with the raw materials (crushed limestone and a small amount of shale), ground into raw feed, and placed in a blending silo. The chemistry of limestone and remaining shale, limited the fly ash addition to 6% of the total raw mix. The raw feed was introduced to the first stage preheater of the cement plant. Typically, as the material travels through the succeeding preheater stages, it encounters hot incoming kiln gases and undergoes substantial preheating before entering the kiln.

5. OPERATIONAL PARAMETERS OBSERVED

Key processing, operational, and environmental parameters were recorded immediately before, during, and after the demonstration – and are discussed in the following sections. It must be noted that a majority of the operational parameters were observed when the composite fly ash “A” was in use, whereas the stack emissions were tested when fly ash “B” was in use.

5.1 Material Handling and Processing

Since the as-received fly ash was a dry, particulate, and free-flowing material, it was extremely easy to pneumatically load, transport to the cement plant, and unload into silos. Furthermore, by virtue of its fine particle size distribution (mean particle size <45 μm), the fly ash did not require pre-grinding prior to blending with the other raw materials at the cement plant.

5.2 Preheater Exit Gas Temperatures

As anticipated, the preheater third and fourth stage exit temperatures rose considerably during the demonstration, but the first and second stage temperature actually declined (Fig 5). This can be attributed to the combustion characteristics of the fly ash. The ash had an endothermic tendency when heated below 550°C (1020°F) (Fig. 3), which contributed to a decrease in the exit gas temperature in the first and second stages. The rise in temperature in third and fourth stages is because of the exothermic nature of the fly ash due to the combustion of carbon above 550°C (1020°F). The comparison of preheaters' temperatures before, during, and after the demonstration is shown in Fig. 5.

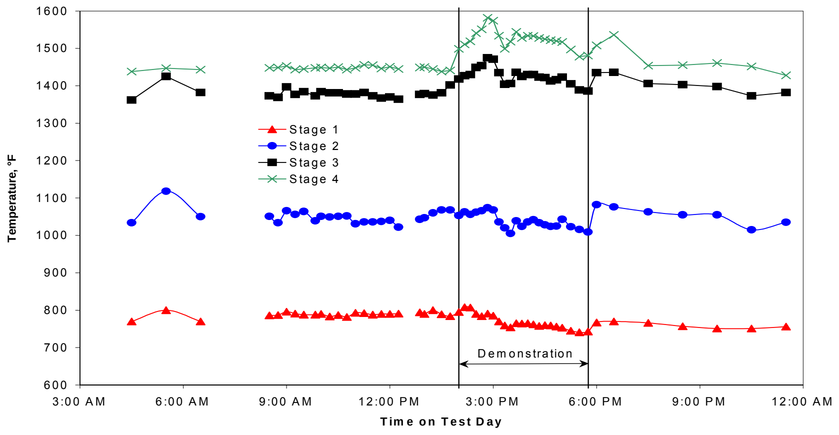


Figure 5. Exit Gas Temperatures in Preheaters

5.3 Improved Calcination

The increased gas temperatures in the final stages of the preheaters improved the calcination of the kiln feed. Feed samples exiting the final stage of the preheater were analyzed for loss on ignition to determine degree of calcination (Table 4). An "additional 20.6%" calcination was realized when the fly ash was in use. This virtually converted the preheater process to a semi-calciner process; and translated to fuel efficiency and improved output.

Table 4. Degree of Calcination at Final Stage Preheater

Loss on Ignition, %			Degree of Calcination, %		
Before	During	After	Before	During	After
16.64	9.62	20.60	51.20	71.79	39.59

5.4 Preheater Tower Pressures

Pressures within the preheater were observed to determine the presence of material build-ups. An increase in exit pressure implies the possibility of blockage due to build-ups, whereas a decrease suggests a clearing up of the pathways for smoother flow of material. During the demonstration, a general decrease was noted. This is probably due, in part, to the higher temperatures in the lower portion of the preheater caused by the combustion of carbon in the fly ash. Preheater pressures are shown in Fig. 6.

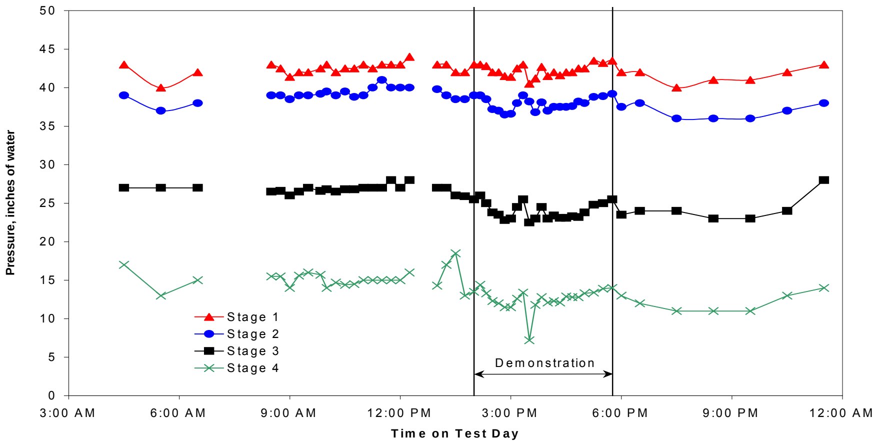


Figure 6. Measured Pressures in Preheaters

5.5 Kiln Feed Rate

During the demonstration, the kiln feed rate increased from approximately 135 tons/hour to 148 tons/hour. After the demonstration, the kiln feed rate returned to a level similar to that of before the demonstration (see Fig. 7).

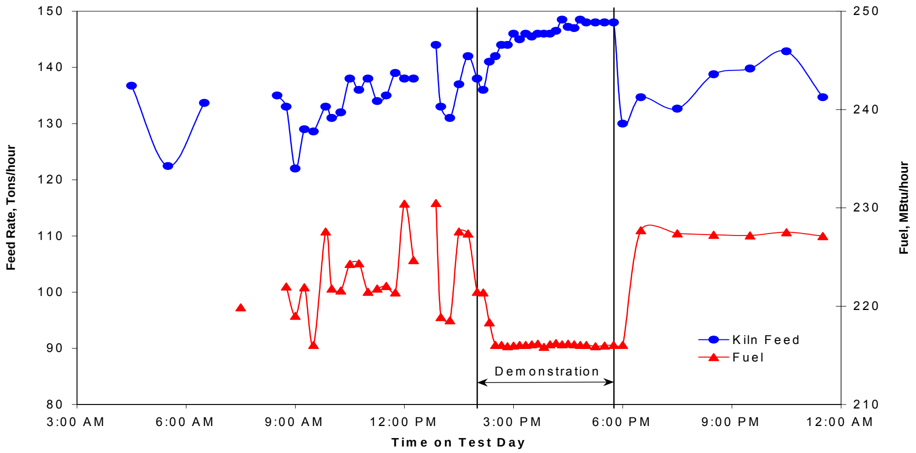


Figure 7. Kiln Feed and Fuel Rate

The increased kiln feed rate translated to an increase of clinker production of nearly 10%. The increase in kiln feed rate is directly attributed to the use of the high carbon fly ash, which increased the calcination of raw feed prior to entry into the kiln. It should also be noted that the additional feed would generate more carbon dioxide, which would increase the load on the I.D. fan. Since the fan was able to accommodate the additional load, it must be concluded that the pressure drop in the preheater probably aided in compensation for this extra CO_2.

5.6 Fuel Feed Rate

Fuel supply was reduced during the demonstration to accommodate for the additional energy provided by high carbon in fly ash. Figure 7 also presents the fuel feed rate into the kiln. Energy savings due to fuel reduction averaged nearly 4% during the demonstration. This represents an approximate fuel saving of 91,000 Btu/ton (22,930 kcal/ton) clinker. A comparison of this figure with the anticipated benefit of 57,300 Btu/ton (14,440 kcal/ton) further confirms the conservatism of this estimate, and attests to the efficiency of heat recovery in actual operation.

5.7 Burning Zone Temperature

During the demonstration, the temperature of the burning zone increased by approximately 200°F (Fig. 8). This was due in part to the residual carbon in the kiln feed that passed through the preheater, but was also due to the actions of the kiln operator. Had the burning zone temperature been kept constant, further fuel savings would have been realized.

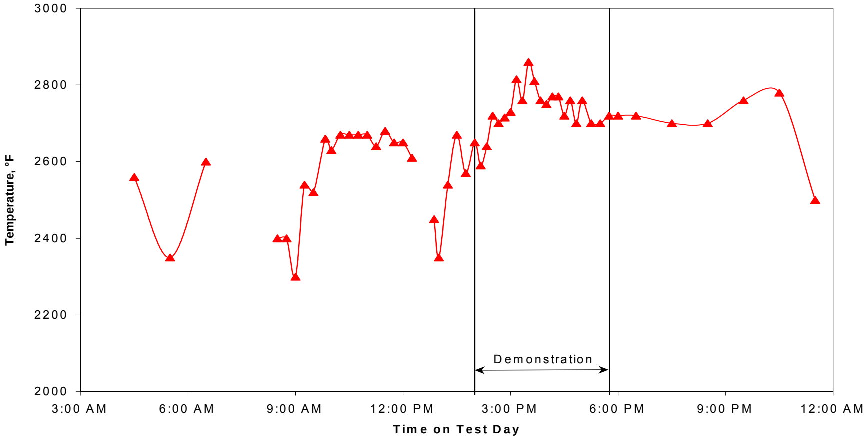


Figure 8. Burning Zone Temperature

5.7 Environmental Considerations

Since, as per the thermal analysis (Fig. 3) no volatiles were present in the fly ash, no emission-related problems were expected to be released into the stack gases. With fly ash A, the level of CO in the stack remained unchanged; there was no change in the stack opacity. Also no formation of detached plumes was observed when the fly ash A was in use. However detailed emissions data was recorded when fly ash B was used (Table 5) [7].

Table 5. Stack Emissions Data during Demonstration with Fly Ash B

Emissions	Before	Demonstration	Change
NO, lb/hr NO, lb/ton clinker	273 3.56	200 2.53	Decrease
CO, lb/hr CO, lb/ton clinker	276 3.60	158 1.99	Decrease
CO_2, %	16.6	16.0	Decrease
H_2O, %	9.1	9.2	Increase
SO_2, ppm	47.0	25.8	Decrease
O_2, % dry	11.2	11.2	No change

As can be seen from the data that the fly ash B, rather facilitated a reduction in the emission levels when used in the raw mix.

6. OVERALL KILN OPERATION

During the demonstration, the kiln run was efficient, trouble-free, and extremely smooth. From an operational standpoint, the demonstration was successful in that the production increased, emissions improved, and fuel economy exceeded expectations; a summary of benefits is given in Table 6.

Table 6. Summary of Operational Parameters Observed

Parameters	Observations	Comments	Operational Impact
Material processing	No pre-grinding required, easy blending and feeding	Dry, free flowing, fine particulate material	Efficient handling, feed preparation, high volume usage
Preheaters temperature	Temperature rose at lower stage	Due to carbon in fly ash	Feed calcination improved
Kiln feed rate	Feed rate increased	Improved calcination	Improved production
Burning zone temp. (BZT)	BZT increased	Because of carbon (C) in fly ash	Fuel saving and efficiency
Fuel Rate	Fuel rate reduced	Improved calcination	Fuel saving
Environments	No CO, no opacity, no detached plumes	Total C combustion, absence of volatiles	Environmentally safe operation
General	Easy fly ash handling No blocking, plugging No snowman formed	Particulate material Uniform raw feed Efficient temp. control	Smooth, glitch free, efficient, and beneficial operation

At present US cement production is about 100 Mt/year. If 5% of the raw feed uses 5% fly ash, this will consume up to 7.5 Mt of presently landfilled ash, reflecting a yearly conversion of >10% waste ash to marketable product.

7. CLINKER AND CEMENT EVALUATION AND QUALITY

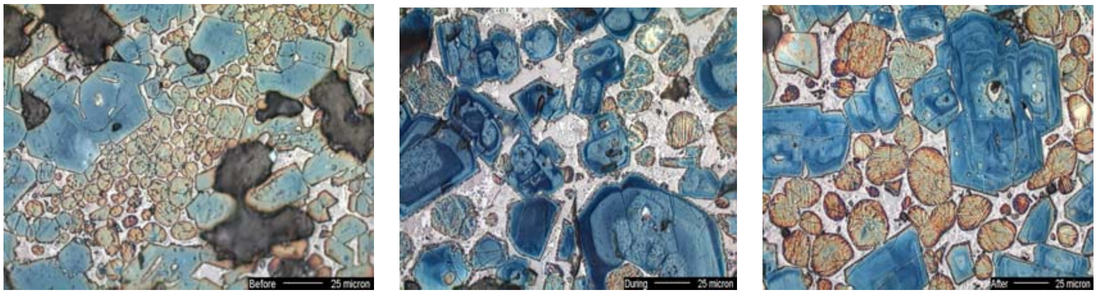
7.1 Clinker Characterization

The data on composition of the demonstration clinker show lower sulfate and alkalies than those produced routinely (Table 7). The demonstration clinker also had a lower free lime than the routine clinkers. Low alkali and low free lime cements are preferred in concrete for better durability properties.

Table 7. Select Oxide Composition of Clinkers, wt. %

Oxide Analysis	Before	Demonstration	After
SiO_2	20.07	21.57	21.05
Al_2O_3	5.45	5.98	6.18
Fe_2O_3	2.49	2.59	2.55
CaO	64.09	64.60	63.80
MgO	2.44	2.47	2.43
SO_3	2.43	0.59	1.71
Na_2O	0.40	0.39	0.42
K_2O	1.28	0.56	1.01
L.O.I.	0.10	0.09	0.10
Free Lime	2.98	0.44	0.54

The microscopical examination on the demonstration clinker confirmed the presence and distribution of all the major phases such as alite, belite, and the interstitials. Some of the belite (C_2S*) crystals are normally sized, but do not have typical lamellae (Fig. 9). This suggests that they may be of the higher-temperature form often helpful in gaining later strength performance.



a) Before b) Demonstration c) After

Figure 9. Photomicrograph of Clinkers Produced

The alite (C_3S) crystals in the demonstration clinker are more deeply etched than in the other two clinkers. This often reflects better hydraulic activity, and can give improved strength development.

7.2 Cement Testing – ASTM C 150 Chemical and Physical Requirements

Data in Table 8 confirms that the demonstration cement meets the standard chemical requirements of ASTM C 150 cement. Similarly, as per the test results in Table 9, the demonstration cement also conforms to the ASTM C 150 physical specifications.

Table 8. Oxide Composition of Cements, wt. %

Oxide Analysis	Before	Demonstration	After
SiO_2	19.45	19.49	19.44
Al_2O_3	5.28	5.37	5.50
Fe_2O_3	2.39	2.59	2.43
CaO	61.36	62.26	61.39
MgO	2.62	2.45	2.41
SO_3	4.08	3.75	4.31
Na_2O	0.49	0.39	0.50
K_2O	0.96	0.75	0.97
L.O.I.	1.84	1.79	1.95
Total	99.26	99.57	99.69
Calculated Cement Compounds			
C_3S*	61	55	49
C_2S	11	14	18
C_3A	10	10	10
C_4AF	8	8	7

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* In cement chemist notation, C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3

Table 9. ASTM C 150 Data on Demonstration Cements

	Before	During	After	ASTM Limits
ASTM C 204 - Fineness, air permeability (Blaine), m^2/kg				
	398	390	402	280 min.
ASTM C 109 - Compressive strength, psi (Mpa)				
3-day	3750 (26)	3650 (25)	3560 (25)	1740 (12) min.
7-day	4490 (31)	4190 (29)	4390 (30)	2760 (19) min.
28-day	5880 (41)	6080 (42)	5670 (39)	4060 (28) min.
ASTM C 191 – Vicat time of set, minutes				
Initial	85	105	90	45 min.
Final	180	210	195	375 max.
ASTM C 185 – Air content, %				
	7.8	8.1	6.4	12 max.
ASTM C 151 – Autoclave expansion, %				
	0.12	0.02	0.05	0.80 max.
ASTM C 390 – Early Penetration, mm				
	10	50	8	None

Data in Table 9 confirm that the physical properties of the demonstration cement are also comparable to those routinely produced at the cement plant.

8. CONCLUSIONS

The commercial demonstration and test data presented in this report have shown that high carbon fly ash can effectively be used as a raw feed component in cement manufacture. The use of high carbon fly ash imparts several operational benefits. Select examples are as follows:

- During the demonstration, the cement plant achieved a fuel savings of nearly 4%, or 91,000 Btu/ton of clinker.
- Production increased by nearly 10%. This resulted from an increased calcination of raw feed in the preheaters due to carbon, increased feed rate, and improved material flow due to pressure drop in the preheaters.
- Emissions remained unchanged (and rather decreased in case of fly ash B); the local environments improved by consuming the unusable fly ash.
- The demonstration cement conformed to the ASTM C 150 specifications, and was also comparable to the routinely produced cements at the plant.

For US cement industry (100 Mt/year), addition of 5% fly ash to raw feed will consume 7.5 Mt ash, reflecting a large-scale conversion of waste to product.

9. ACKNOWLEDGEMENTS

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