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Project Title: **USE OF HIGH-CARBON ILLINOIS COAL FLY ASH IN PORTLAND CEMENT MANUFACTURING**

ICCI Project Number: 98-1/3.1C-2
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ABSTRACT

A two-phase project on the use of high-carbon Illinois coal fly ash as a raw feed ingredient for producing portland cement was undertaken. Such fly ashes can replace shale and clay in the raw feed, and the carbon will provide supplementary fuel value.

During Phase I, several Illinois fly ash samples were collected and characterized. Three fly ashes, owing to their chemical compositions and high carbon contents, were selected for testing as a raw feed component in cement manufacture. Fly ashes were procured from the City Water Light and Power, Vermilion, and Grand Tower power plants.

Raw materials and kiln feeds from the Lone Star, Illinois Cement, Dixon-Marquette, and Lafarge cement plants were obtained for parallel testing and comparison. These four cement plants represent all of the cement manufacturing capacity in Illinois.

Based on chemical analyses and relative proximity, fly ashes were paired with cement plants. Seven mix formulations incorporating fly ash with the cement plant raw materials were prepared and burned to form clinker. Clinkers were subsequently analyzed by chemical and physical methods. Tests confirmed that clinkers produced from the fly ash-containing mix formulations were comparable in characteristics to those produced directly from the respective kiln feeds. Results suggest that the fly ash can potentially improve the burnability of the kiln feed.

During Phase II, one optimum fly ash raw mix formulation for each cement plant, along with the companion kiln feed, was burned in CTL's pilot scale rotary kiln to form clinker. Clinkers were subsequently analyzed by chemical and physical methods. Tests confirmed that the clinkers produced from the fly ash-containing raw mixes were comparable in characteristics to those produced directly from the respective kiln feeds.

Cements were produced from clinkers for evaluation in accordance with selected ASTM C 150 specifications. Results indicated that cements made from fly ash-containing clinkers meet the requirements of an ASTM C 150 Type I Portland cement, and had improved compressive strength development in comparison to control clinkers.

Estimated energy savings from incorporation of Illinois high carbon fly ash in the kiln feed ranged from 122,100 to 298,940 Btu per ton of clinker, a 3.6 to 8.8% savings.

EXECUTIVE SUMMARY

This project consisted of a two-phase study to evaluate the potential for using Illinois high carbon fly ash as a partial raw feed and fuel substitute. During Phase I, samples of high-carbon fly ashes from Illinois power plants, including those in close proximity to the Illinois cement plants were collected. Several fly ashes were received and tested for their chemistry and compound compositions (including the unburned carbon content based upon the loss-on-ignition and thermal analyses).

Likewise, typical raw materials (limestone, shale, clay, sand, etc.) from the four Illinois cement plants- Lone Star at Oglesby, Dixon-Marquette at Dixon, Illinois at LaSalle, and Lafarge at Joppa, were also collected. Regular production kiln feeds from these plants were also obtained as the control or target materials.

The fly ash samples and the raw materials including the target kiln feeds were analyzed for their contents of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, alkalies, etc., and loss-on-ignition (LOI). The fly ashes were examined for their carbon content to determine the potential fuel value. Three fly ashes were selected based on their chemical composition, carbon contents, and lack of volatile release at low temperature (to avoid emission problems). These were the ashes obtained from the CWLP, Vermilion, and Grand Tower power plants.

Seven cement raw mixes were formulated using the raw materials with the fly ashes. The use of fly ash was maximized as the principle source of alumina, silica, and iron. Insofar as possible within compositional constraints, the mixes were to consist of fly ash and limestone only. Minor amounts of corrective materials were added to the raw mix, only if necessary to adjust the lime saturation factor, silica modulus, and other burnability factors. Fly ashes replaced between 4.7 and 9.0 percent of the current raw mix of the cement plant kiln feeds.

Each raw mixture was press-pelletized and subjected to firing at temperatures sufficient to complete clinkering. The clinkering temperature was typically 1450°C with a residence time of approximately one-hour. For burnability tests, two additional temperatures of 1350°C and 1400°C were included. The clinkers were tested for the appropriateness of the major phases by X-ray diffraction (XRD), X-ray fluorescence (XRF), and optical microscopy. The Franke free-lime method was used to determine free lime in the clinkers. The data were compared and contrasted with those of the target clinkers made directly from the kiln feed.

The tests confirmed that the clinkers produced from the fly ash containing mix formulations were comparable in characteristics to those produced directly from the respective kiln feeds. The tests have also indicated significant energy benefits of the carbon contents in fly ashes. For example, a 5% replacement by the CWLP fly ash would contribute nearly 50,000 Btu/ton of clinker; a 9% Vermilion fly ash replacement would supplement over 115,000 Btu/ton clinker, and a 9% replacement by Grand Tower fly ash would give nearly 275,000 Btu/ton clinker of produced. Furthermore, there was no evidence of any adverse effects of carbon in fly ash on the release of volatile matter when

tested for thermal behavior by differential scanning calorimetery (DSC). Therefore, no emission problems are expected from the incorporation of these high-carbon fly ashes.

During Phase II, one fly ash raw mix formulation was selected for each of the Illinois cement plants. Due to a material shortage, additional CWLP fly ash was procured. All raw materials were reanalyzed and the four fly ash-containing raw mixes were formulated. The fly ash-containing raw mixes along with companion kiln feeds from the cement plants (controls) were pelletized and burned in CTL's pilot scale rotary kiln. The burning temperature was in excess of 1400°C, with an estimated residence time of 40 minutes. Free lime content was checked periodically through XRD analyses. Due to the limitations of the kiln, it was not possible to measure the fuel savings due to the fly ash.

Resulting clinkers were analyzed by XRF, XRD, and optical microscopy. Fly ash and control clinkers had nearly identical chemical constituents. Optical microscopy showed comparable clinker microstructure, evidencing comparable quality. The grindability of the clinkers was nearly identical.

All cements made from the fly ash-containing and control clinkers complied with the requirements for a Type I Portland cement, as specified in ASTM C 150, "Standard Specification for Portland Cement". Additionally, cement produced from fly ash containing clinkers showed improved compressive strength development over those of the companion control clinkers.

The estimated energy savings due to the incorporation of Illinois high-carbon fly ash in the kiln feeds, as burned in the pilot scale production of clinker ranged from 122,100 to 298,940 Btu per ton of clinker. Given that the average preheater/precalciner cement plant consumes approximately 3.4 MBtu of fuel energy per ton of clinker produced, the estimated energy savings range from 3.6 to 8.8 percent. This represents a significant energy savings.

OBJECTIVES

The objective of the project was to convert high-carbon Illinois fly ash into portland cement by using it as an ingredient in the raw kiln feed. In cement, the fly ash should serve as a raw material by replacing shale and clay as a source of alumina, silica, and iron. The carbon content of the fly ash should also serve as a partial fuel substitute during the kiln burning process of producing portland cement clinker. In so doing we expect to realize several interrelated economical, environmental, and product benefits, as follows:

- The cement plants should be able to save between 50,000 to 275,000 Btu per ton of clinker in fuel energy from the energy value of the fly ash.
- The quality of cement produced from the fly ash replacement should be fully comparable with that produced from the original raw materials, when tested as per the methods required in the ASTM C 150 specifications for portland cement.
- Use of fly ash can potentially result in low-alkali cements and lower alkali kiln dust, primarily because the fly ashes contain lower alkalies than the clays and shales they replace. Low-alkali cements are in high demand for providing reduced alkali-silica reactivity, whereas, the low alkali dusts are more easily recycled.
- When the use of fly ash as an appropriate replacement is successfully implemented, the cement plant should be able to realize a noticeable improvement in production owing to enhanced burnability during the kiln operation.

INTRODUCTION AND BACKGROUND

There are nearly 30 power plants in the State of Illinois that annually consume more than 30 million tons of coal and produce over three million tons of coal combustion residues each year. Of these residues, less than 10 percent is used in commercial products. The implementation of the Clean Air Act to reduce NO_X emissions at coal-fired power plants will increase the production of combustion residues, with a significantly higher unburned carbon content, potentially almost tripling the present levels in fly ash.

Further, by virtue of their diverse chemical compositions, the fly ashes can be susceptible to groundwater leaching and possible contamination. The potential pollution scenarios, pressure for environmentally safe disposal, and the “landfill crisis,” combined with political opposition to new landfill sites, has exacerbated waste disposal problems more than previously anticipated, posing a technical challenge to develop safe alternative disposal routes.

Traditionally, in cement operations, shale, clay, slate, sandstone, and mill-scale are used to provide necessary silica, alumina, and iron contents for the kiln feed. Since fly ash is rich in these compounds, it should be able to be used in the formulation of cement raw feed. The use of fly ash should also enhance the burnability of the kiln feed because of its finer particle size and favorable reactivity with lime, which is the major component in the feed.

During this project, cements were formulated using cement plant raw materials and high carbon Illinois fly ash. The cements thus produced were evaluated for compliance with the ASTM C 150 specifications for compressive strength, soundness, durability, and other performance related properties, for suitability in general purpose construction. We anticipated that, owing to the low alkali levels of raw feed made with the fly ash, the cements would have low alkali contents, to give reduced alkali-silica reactivity as compared to the control cement made from the traditional kiln feed.

This approach will promote an efficient and cost-effective utilization of Illinois fly ash and result in several technical, economical, and environmental benefits as follows:

- A 10% use of fly ash in the four cement plants in Illinois (combined clinker capacity[*] of 2.5 million tons per year), would consume approximately 387,000 tons of fly ash each year. This would significantly increase the consumption of fly ash in commercial products. This “waste-to-product” approach will generate a saleable product while reducing fly ash disposal to the landfills in Illinois.

- The four cement plants in Illinois can conserve more than 40,000 tons per year of coal by using 10% fly ash containing 10% carbon.

- Being a finely divided and free flowing material, the fly ash will be amenable to easy blending with the raw feed without pre-grinding. The fly ash may be added to the classifier on the raw mill, which will subject only the coarse fraction to grinding.

- Fly ash, which normally possesses high reactivity with lime at high temperatures, should facilitate an easier reaction and reduced residence time required for clinkering in the kiln. This has the potential to permit increased kiln production or reduced energy consumption.

- The cements will normally have lower alkali contents than the cements produced using the normal raw materials, and as such will have competitive advantages for use in concrete due to their reduced alkali-silica reactivity with aggregates.

- A reduced alkali kiln feed will allow a cement plant to reduce the amount of cement kiln dust that must be discarded.

To achieve these goals a two-phase project was proposed. Phase I was primarily a bench-scale parametric study on the formulation of kiln feeds containing fly ash, and comparing the properties of clinkers made with fly ash against those made with the kiln feeds from the commercial Illinois cement plants. Phase II entailed pilot scale production of clinkers from the optimum fly ash raw mix formulation for each cement plant along with the companion non-fly ash-containing kiln feed. Clinkers were subsequently analyzed by chemical and physical methods to ensure that fly ash kiln feeds produce characteristics

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[*] Approximately 1.55 tons of raw material are required to produce 1 ton of clinker.

comparable to those produced directly from the respective kiln feeds. Cements were produced from clinkers for evaluation in accordance with ASTM C 150 specifications.

EXPERIMENTAL PROCEDURES

Task 1. Materials Procurement

Fly ash samples from several coal-fired power plants in Illinois were procured. These plants included Havana, Marion, Hennepin, Hurtonville, Meridosia, Wood River, CWLP, Grand Tower, and Vermilion.

Likewise, samples of raw materials from the four Illinois cement plants, i.e., Lone Star at Oglesby, Illinois Cement at LaSalle, Dixon-Marquette at Dixon, and Lafarge at Joppa, were also acquired. Additionally, kiln feeds from these cement plants were also obtained.

Task 2. Materials Characterization

The fly ash samples were characterized for their chemical composition by X-ray fluorescence spectroscopy (XRF) for content of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, etc. Gravimetric methods were used for moisture and loss-on-ignition.

The fly ashes with higher loss-on-ignition (suggesting high unburned carbon contents) were further evaluated by differential scanning calorimetry (DSC) method. The techniques permitted an evaluation of how much combustible matter (primarily unburned carbon in this case) was present in the ash. This technique also determined the temperature at which the volatile matters are released, whether they burn or escape combustion, and the effect of atmosphere on the behavior of these organic species.

The raw materials and kiln feeds from the four Illinois cement plants were analyzed for major oxides by X-ray fluorescence (XRF), to ensure that accurate analyses are available for mix design work and bench scale burns.

Task 3. Formulation of Raw Kiln Feeds

The chemical composition of the raw materials, the fly ashes, and the four kiln feeds were examined for compatibility with that of the raw materials of the cement plants. Based on their chemical compositions and the amount of carbon content (suggested by a high LOI and high heat values), and most critically, the economics of transport and reuse factor, three fly ashes were chosen for the formulation of raw mixes.

Mix design calculations were carried out to achieve the desired clinker composition with respect to key cement-manufacturing parameters such as the silica ratio, alumina modulus, and lime saturation factor and the consequent content of the major clinker phases, including the tricalcium silicate (C_3S[*]), dicalcium silicate (C_2S[*]), tricalcium aluminate (C_3A[*]), and tetracalcium aluminoferrite (C_4AF[*]).

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[*] In cement notation, C = CaO, A = Al_2O_3, S = SiO_2, F = Fe_2O_3, and H = H_2O

Task 4. Bench-Scale Production and Evaluation of Clinkers

The seven raw mixes formulated above were interground for complete mixing. These mixes along with the four plant-generated kiln feeds were pelletized. The pellets were fired at 1000°C for 30 min., then at 1350°C, 1400°C, and 1450°C for 45 minutes to produce clinkers. The clinkers were evaluated and compared with the clinkers produced from the kiln feeds (target mix).

The eleven clinkers (seven from the mix formulations and four from the kiln feeds) produced above were examined for the major clinker phases of C_3S, C_2S, C_3A, C_4AF by XRD, XRF, and microscopical analyses. Bogue analyses and Franke free-lime tests were conducted to determine major clinker phases and free lime in order to assess the burnability of the fly ash-containing clinkers while comparing them with those of the target clinkers. The burnability is generally termed as the ease with which the fly ash reacts with the lime-rich kiln feed.

Task 5. Pilot-Scale Raw Mix Preparation

Based on the results of Task 4, one optimum raw mix formulation containing fly ash was selected for each cement plant. Large batches of raw feed were prepared by intergrinding the ingredients in a ball mill to a specific fineness. The four raw mixes and the four control kiln feeds (one from each Illinois cement plant) were then pelletized for introduction into the pilot-scale rotary kiln.

Task 6. Pilot-Scale Burns

The four pelletized raw mixes and four kiln feeds were burned into cement clinker in CTL's pilot-scale rotary kiln. Periodic checking of the free lime content of the clinker by XRD was done to ensure completeness of burning. As a note, the free lime contents were expected to be in excess of 1%. This is typical of pilot-scale rotary kiln produced clinkers inasmuch as the residence time is necessarily short by production kiln standards.. Approximately 20 to 30 lbs. of each clinker were produced from these burns.

Task 7. Characterization/Evaluation of Clinkers

The physical and chemical properties of the eight clinkers were characterized by XRD, XRF, optical microscopy, and measurement of the grindability. A comparison of the properties of the clinkers from the raw mixes containing fly ash to that of the control kiln feeds (from cement plants) was sought.

Task 8. Production of Cement

Cements were prepared from each clinker by grinding in a ball mill with an appropriate amount of gypsum and plaster, proportioned according to clinker aluminate content and other parameters, to an approximate Blaine fineness of 350 m^2/kg. Care was exercised to obtain finenesses, sulfate phases, and particle size distributions as similar as possible to those of typical commercial cements.

Task 9. Testing of Cements

The eight cements were subjected to a series of standardized tests to ensure that they conformed with ASTM C 150, "Standard Specification for Portland Cements". ASTM C 150 includes the measurement of the compressive strength at 3, 7, and 28 days, autoclave expansion, air entraining potential, and time of set. Additional testing for early stiffening potential and alkali-silica reactivity were anticipated to compare with the proprieties of the cements produced with fly ash to that of the cements produced from the cement plant materials.

RESULTS AND DISCUSSION

Relevant results from the bench scale testing (Phase I) and pilot-scale testing (Phase II) are presented and discussed in this section. Results of the Phase I work is presented below.

PHASE I

Cement Plant Raw Materials

Raw materials were procured from the four cement plants in Illinois. Table 1 presents the breakdown of the raw materials received from the cement plants. These materials were analyzed by XRF for subsequent use in mix design formulations.

Table 1. Raw materials from the cement plants

Cement Plant and Location	Raw Materials Received
Lone Star, Oglesby	Low and high limestones*, bottom ash, sand
Illinois Cement, LaSalle	Limestone, shale, sand, fly ash
Dixon-Marquette, Dixon	Low and high MgO limestones, clay, sand, and mill scale
Lafarge, Joppa	Limestone, clay, sand, EEI ash, mill scale

*Low limestone means low in CaO content, and high means high in CaO content.

Fly Ash Characterization, Compatibility, and Fuel Values

The chemical compositions of the three fly ashes selected for testing are presented in Table 2. Results confirm SiO_2, Al_2O_3, and Fe_2O_3 as their major components. Unburned carbon content is a major constituent of the loss-on-ignition (LOI).

The differential scanning calorimetry (DSC) tests conducted on the fly ashes revealed that the ashes have reasonable heat values and no emission-related volatile matter should be released from these ashes, when used in the kiln feeds.

The DSC plots for the ashes are shown in Figures 1 through 3. In all cases, results (lack of peaks) from room temperature to nearly 500°C suggests an extremely low volatile activity in this temperature range. Thus, very little volatile matter is anticipated to be released in stack emissions (from the kiln) during combustion. Typically, the volatile matter released above 500°C is burned in the kiln and is completely destroyed.

The heat values calculated from the exothermic peak in the DSC analyses represent significant energy savings. Since the peaks were still incomplete at the end of the DSC runs, appropriate estimations were made to account for the missing peak area to arrive at a reasonable total heat value of the fly ash. The estimated heat values of the CWLP, Vermilion, and Grand Tower fly ashes were 331, 419, and 984 Btu/lb., respectively.

Table 2. The XRF analyses of the three fly ashes (% wt.)

Oxide	CWLP, wt%	Vermilion, wt%	Grand Tower, wt%
SiO_2	51.45	48.20	41.45
Al_2O_3	12.90	23.38	17.63
Fe_2O_3	17.00	10.22	18.73
CaO	3.37	3.95	1.71
MgO	0.67	1.12	0.71
SO_3	0.59	0.80	0.30
Na_2O	2.20	1.39	0.12
K_2O	2.00	2.37	2.14
TiO_2	0.94	1.08	0.87
P_2O_5	0.15	0.15	0.26
Mn_2O_3	0.05	0.12	0.03
SrO	0.03	0.03	0.02
L.O.I (950°C)	7.98	5.70	14.88

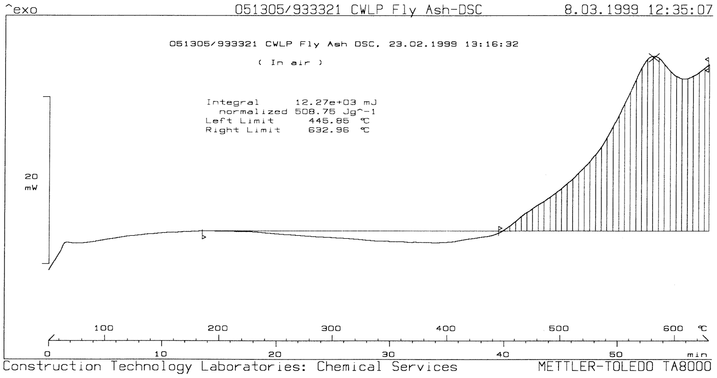

Figure 1. DSC plot for CWLP fly ash

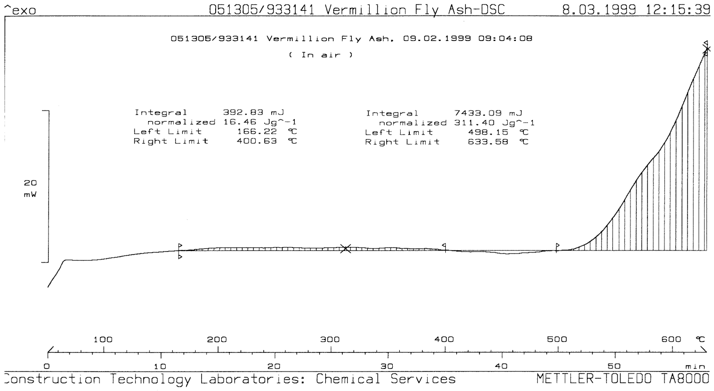

Figure 2. DSC plot for Vermilion fly ash

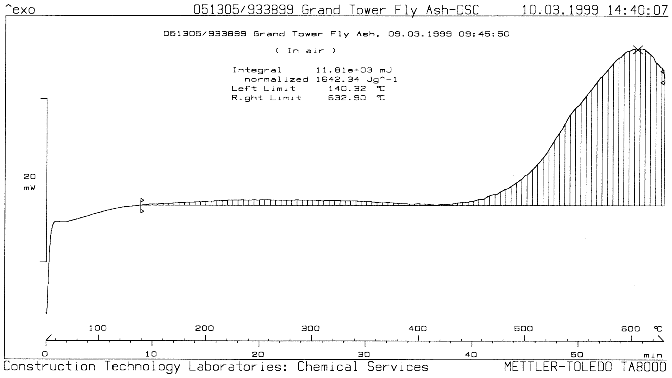

Figure 3 DSC plot for Grand Tower fly ash

Pairings and Bench Scale Mix Designs

Pairings of the fly ashes with the cement plants was based on the chemical composition and compatibility of the raw materials and fly ashes with respect to the four kiln feeds. The economics of transport and use factor of the fly ashes in the raw mixes was also considered. Pairings are presented in Table 3.

Table 3. Pairings of cement plants and fly ashes

Mix No.	Cement Plant	Fly Ash
1	Lone Star	CWLP
2	Lone Star	Vermilion
3	Dixon-Marquette	CWLP
4	Dixon-Marquette	Vermilion
5	Illinois Cement	CWLP
6	Illinois Cement	Vermilion
7	Lafarge	Grand Tower

Tables 4 through 7 present the seven mix formulations and their companion kiln feeds (the target formulations). As shown in the tables, significant amounts of fly ash are included. Mix design formulations were made to maximize the use of fly ashes in replacing clay, shale, sand, and mill scale in the kiln feeds. Calculations considered the key cement-manufacturing parameters such as the silica ratio[†], alumina modulus[‡], and lime saturation factor[*] and the consequent content of the major clinker phases, including the tricalcium silicate (C_3S), dicalciumsilicate (C_2S), tricalcium-aluminate (C_3A), and tetracalciumaluminoferrite (C_4AF). These are important cement-manufacturing parameters as they control the ease of burning leading to the completion of clinkering and formation of the desired clinker phases. Table 8 outlines the calculated values of these

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[†] Silica Ratio = S / (A + F)

[‡] Alumina Modulus = A / F

[*] Lime Saturation Factor = (100 * C) / (2.85 + 1.65 * A + 0.35 * F) if the Alumina Modulus > 0.64
= (100 * C) / (2.85 + 1.1 * A + 0.7 * F) if the Alumina Modulus ≤ 0.64

parameters for the mix formulations and their comparison with the target mix (current kiln feed). Typical ranges are also quoted for cross-reference. Note that a small amount of pre-calcined fly ash was added to the kiln feeds to represent the residual ash from the kiln fuel combustion.

As indicated in Table 8, the parameters for all the mix formulations were comparable to those of the target mixes and fairly close to the preferred ranges for clinkering.

Table 4. Lone Star mix formulations

Material	Kiln Feed, wt%	Mix No. 1, wt%	Mix No. 2, wt%
Low limestone	80.3	85.3	54.5
High limestone	13.6	8.6	38.0
Bottom ash	4.3	—	—
Sand	1.8	1.0	1.6
CWLP fly ash	—	5.1	—
Vermilion fly ash	—	—	5.9

Note: Low limestone has a low CaO content. High Limestone has a high CaO content.

Table 5. Dixon-Marquette mix formulations

Material	Kiln Feed, wt%	Mix No. 3, wt%	Mix No. 4, wt%
Low MgO limestone	49.9	49.8	48.7
High MgO limestone	39.0	39.0	40
Clay	9.2	5.4	—
Sand	0.9	0.8	2.2
Mill scale	1.0	—	0.3
CWLP Fly ash	—	5.0	—
Vermilion Fly ash	—	—	8.8

Note: Limestones were either high or low in magnesium oxide content.

Table 6. Illinois Cement mix formulations

Material	Kiln Feed, wt%	Mix No. 5, wt%	Mix No. 6, wt%
Limestone	88.3	88.4	89.0
Shale	7.0	6.9	—
Sand	0.7	—	2.0
Fly ash	4.0	—	—
CWLP Fly ash	—	4.7	—
Vermilion Fly ash	—	—	9.0

Table 7. Lafarge mix formulations

Material	Kiln Feed, wt%	Mix No. 7, wt%
Limestone	84.7	85.2
Clay	4.7	2.3
Sand	4.5	3.5
EEI ash	4.8	—
Mill scale	1.3	—
Grand Tower fly ash	—	9.0

Calculated energy savings, based on energy content calculations from DSC, are shown in Table 9. The contribution of heat from the high carbon fly ash is significant and can result in sizable fuel savings.

Table 8. Silica ratio, alumina modulus, and lime saturation factor for mix formulations

Cement Plant	Mix	Parameters		
		Silica Ratio	Alumina Modulus	Lime Saturation Factor
Lone Star	Target	2.35	2.10	101
	No. 1	2.37	1.72	99
	No. 2	2.29	2.28	99
Dixon-Marquette	Target	2.45	1.83	96
	No. 3	2.42	1.73	96
	No. 4	2.31	1.85	97
Illinois Cement	Target	2.41	2.13	97
	No. 5	2.26	1.62	97
	No. 6	2.33	2.20	97
Lafarge	Target	2.74	1.45	97
	No. 7	2.64	1.41	97
Limiting Ranges		***1.9 to 3.2***	***1.0 to 2.7***	***66 to 102***
Preferred Ranges		***2.3 to 2.7***	***1.3 to 1.6***	***92 to 96***

**Table 9. Calculated heat contribution (Btu/ton of clinker)
during production of lab scale clinkers**

Lone Star		Dixon-Marquette		Illinois Cement		Lafarge
Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	Mix 7

52,280	76,690	51,250	114,390	48,180	116,990	274,470

Evaluation of the Bench Scale Clinkers

The clinkers produced (at 1450°C) from the above mix formulations were compared with those prepared from the respective kiln feeds. Clinkers were analyzed by XRD, XRF, optical microscopy to identify and quantify the major phases, and by the Franke free lime test to assess burnabilty.

Table 10 presents the major phases determined by XRF analyses and Bogue calculations. Phase distributions of the fly ash containing clinkers were comparable to the respective target clinkers. These results were confirmed by XRD and optical microscopy.

Table 10. Phases (% wt.) in clinkers prepared at 1450°C from the mix formulations

Cement Plant	**Mix**	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
Lone Star	Target	52	22	12	9
	No. 1	59	15	10	10
	No. 2	59	15	12	9
Dixon-Marquette	Target	46	27	11	10
	No. 3	42	29	11	10
	No. 4	46	25	11	10
Illinois Cement	Target	62	13	11	9
	No. 5	65	12	8	11
	No. 6	62	14	8	11
Lafarge	Target	69	8	8	10
	No. 7	63	15	7	10

The burnability of the clinkers was assessed by burning at temperatures of 1350, 1400, and 1450°C and analyzing the resulting free lime content. Low free lime contents are desired. Table 11 presents the free lime contents of clinkers produced at different temperatures. Results confirm that the addition of fly ash improved the burnability.

Table 11. Free lime content (% wt.) of clinkers prepared at various temperatures

Cement Plant	Mix	Clinkering Temperature		
		1350°C	1400°C	1450°C
Lone Star	Target	1.44	0.68	0.18
	No. 1	1.12	0.64	0.11
	No. 2	1.10	0.60	0.11
Dixon-Marquette	Target	2.90	0.98	0.07
	No. 3	0.42	0.10	0.07
	No. 4	0.57	0.20	0.07
Illinois Cement	Target	3.04	2.25	0.86
	No. 5	1.98	1.36	0.51
	No. 6	1.43	1.50	0.55
Lafarge	Target	4.84	3.14	1.82
	No. 7	4.20	2.50	2.03

PHASE II

Pilot Scale Raw Mixes

For the scale-up to the pilot scale, one optimum raw mix formulation containing fly ash was selected for each cement plant. Raw materials were reanalyzed to confirm original analyses. Mix formulations were slightly modified based on the analyses and are presented in Tables 12 through 15, along with the cement plant kiln feeds.

As a note, during Phase I, we exhausted our supply of CWLP fly ash. Additional CWLP fly ash was procured. The fly ash was reanalyzed and found to have a nearly identical chemical content (on the ignited basis) with that of the original CWLP fly ash. However, the carbon content was found to be increased from 7.98 to 19.96 wt.%. The resulting energy content from DSC analyses was calculated to be 952 Btu/lb. Table 16 presents the calculated fuel savings from the pilot-scale mix designs.

Table 12. Lone Star mix formulations (wt. %)

Material	Control	Fly Ash
Low CaO limestone	80.3	53.0
High CaO limestone	13.6	41.0
Bottom ash	4.3	—
Sand	1.8	1.5
CWLP fly ash	—	4.5

Table 13. Dixon-Marquette mix formulations (wt. %)

Material	Control	Fly Ash
Low MgO limestone	49.9	48.0
High MgO limestone	39.0	39.4
Clay	9.2	—
Sand	0.9	2.2
Mill scale	1.0	0.3
Vermilion Fly ash	—	10.1

Table 14. Illinois Cement mix formulations (wt. %)

Material	Control	Fly Ash
Limestone	88.3	88.5
Shale	7.0	—
Sand	0.7	2.1
Fly ash	4.0	—
Vermilion Fly ash	—	9.4

Table 15. Lafarge mix formulations (wt. %)

Material	Control	Fly Ash
Limestone	84.7	83.7
Clay	4.7	2.0
Sand	4.5	4.5
EEI ash	4.8	—
Mill scale	1.3	—
Grand Tower fly ash	—	9.8

Table 16. Estimated energy contribution and savings from fly ash in pilot scale clinkers

Mix	Energy Contribution, Btu/ton of clinker	Energy Savings*, percent
Lone Star	132,800	3.9
Dixon-Marquette	131,190	3.9
Illinois Cement	122,100	3.6
Lafarge	298,940	8.8

* Based on 3.4 MBtu of fuel energy per ton of clinker.

Pilot Scale Raw Mix Preparation and Burns

Large batches of fly ash containing raw mixes were prepared by crushing raw materials passing a 30 mesh sieve, blending, and intergrinding the ingredients in a ball mill to pass a 200 mesh sieve. The four raw mixes and the four control kiln feeds (one from each Illinois cement plant) were then pelletized for introduction into the pilot-rotary kiln. Photo 1 presents a pelletized control kiln feed prior to burning and a typical clinker.

Pelletized Raw Mix Resulting Clinker

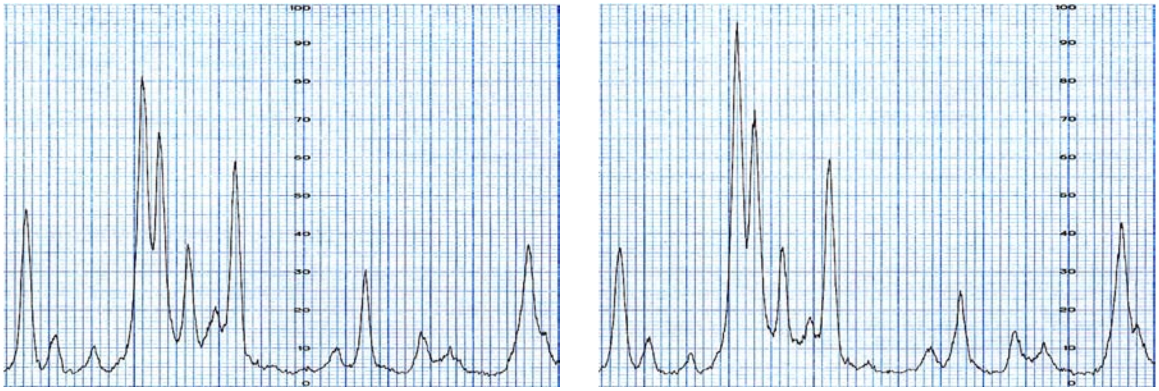
Photo 1. Pelletized raw mix prior to burning and the resulting clinker

Raw mixes and kiln feeds were burned into clinker in our pilot-scale rotary kiln with natural gas as a fuel. The approximate burning temperature was in excess of 1400°C. Residence time in the kiln was estimated to be approximately 40 minutes. During burning of the raw mixes, periodic checking of the phases and free lime content of the clinker was performed. Monitoring of kiln emissions or the fuel use was not possible.

Pilot Scale Clinker Evaluation

Clinkers produced from the four raw mixes and control kiln feeds were characterized by XRD, XRF and optical microscopy. Free lime content was measured in addition to the grindability of the clinkers to determine the effect of fly ash in the raw feeds.

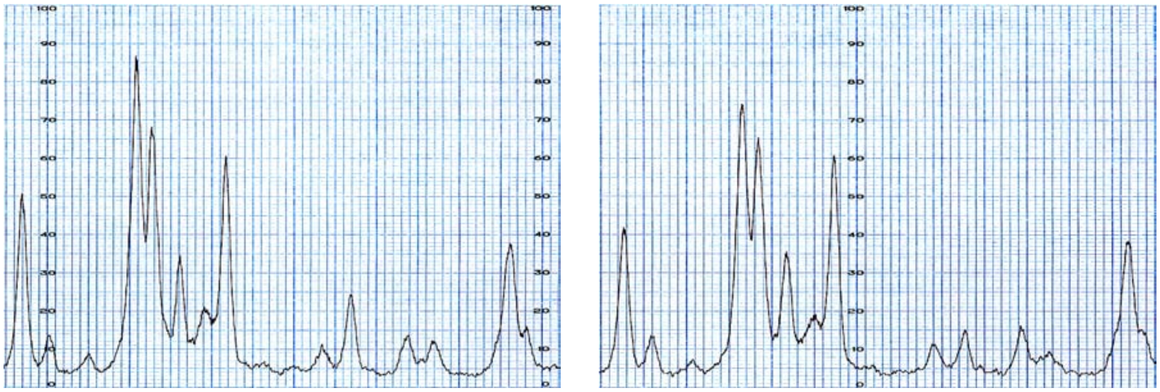
The XRD patterns shown in Figures 4 through 7 confirm the formation of major phases in clinkers prepared from all mix formulations. The peak intensities of the major phases in the fly ash containing clinkers are comparable with those of the target clinkers. The x-axis in the XRD patterns is the 2-theta angle and the y-axis is the intensity. The 2-theta angles for major clinker phases in the XRD patterns are: C_3S = 32.2°, C_2S = 41.2°, C_3A = 33.15°, C_4AF = 33.8°, and free lime = 37.4°. In Figures 4 through 7, the XRD patterns start at 29° 2-theta (left side) and end at 43° 2-theta (right side). Each darker vertical grid line represents a 1° 2-theta angle.



Control Mix

Fly Ash Mix

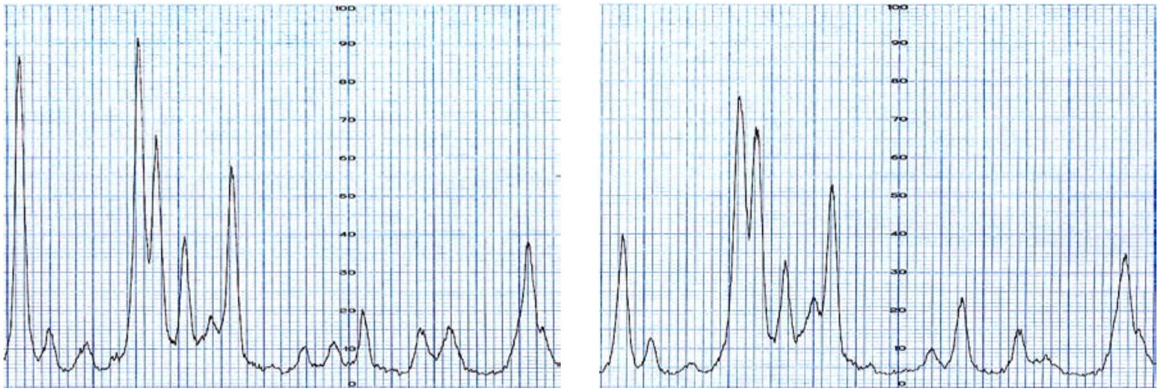
Figure 4. XRDs (2-theta from 29° to 42°) of Lone Star clinkers



Control Mix

Fly Ash Mix

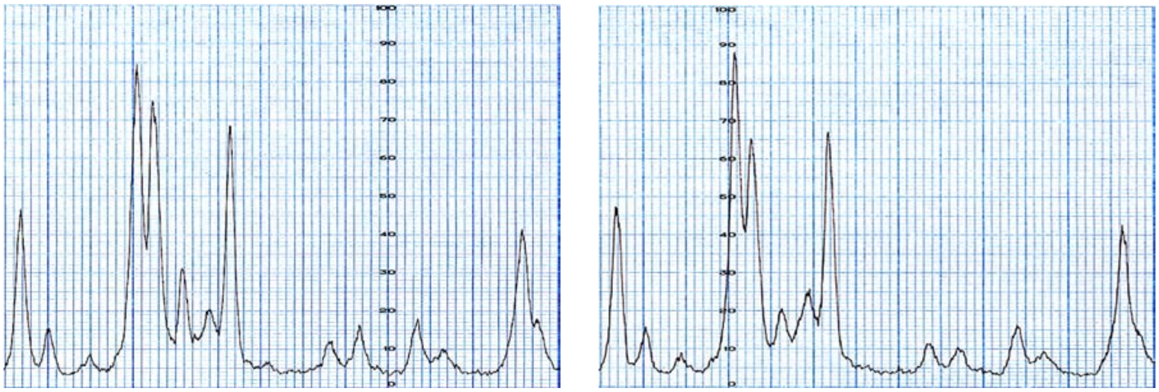
Figure 5. XRDs (2-theta from 29° to 42°) of Dixon-Marquette clinkers



Control Mix

Fly Ash Mix

Figure 6. XRDs (2-theta from 29° to 42°) of Illinois Cement clinkers



Control Mix

Fly Ash Mix

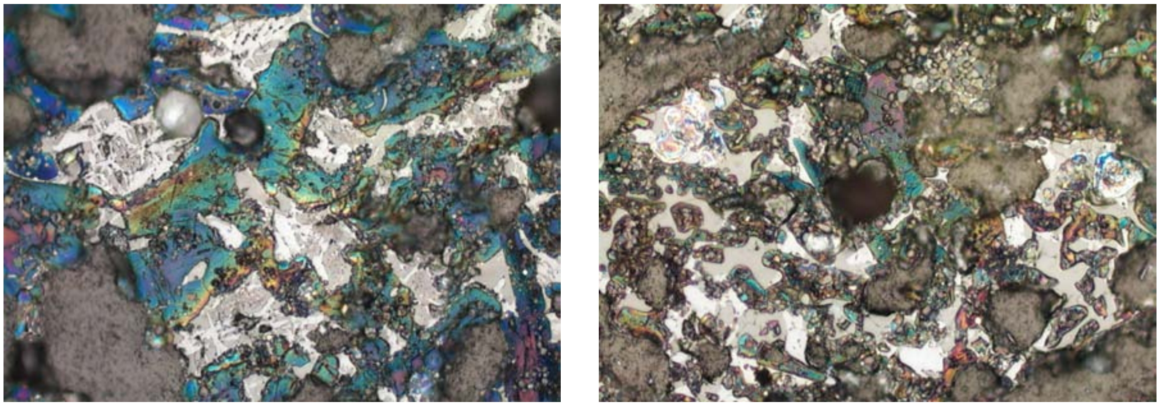
Figure 7. XRDs (2-theta from 29° to 42°) of Lafarge clinkers

The XRF analyses, Bogue potential compound calculations, and free lime contents are shown in Table 17. Results confirm the formation of major phases in clinkers prepared from all mix formulations. Fly ash-containing clinkers are similar (chemically) to the control clinkers.

Table 17. Phases (% wt.) in pilot-scale produced clinkers

Analyte	Lone Star		Dixon-Marquette		Illinois Cement		Lafarge	
	Control	Fly Ash	Control	Fly Ash	Control	Fly Ash	Control	Fly Ash
SiO_2	21.75	22.35	21.16	20.92	21.29	21.22	22.03	21.64
Al_2O_3	6.08	5.57	5.55	5.78	5.82	5.95	5.12	4.94
Fe_2O_3	2.94	3.13	3.06	3.04	2.96	3.13	3.37	3.34
CaO	66.92	65.65	65.97	65.46	64.54	65.94	65.38	65.74
MgO	1.99	2.03	3.51	4.09	4.14	2.98	3.13	3.56
SO_3	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02
equiv. Na_2O	< 0.02	0.08	< 0.02	0.01	0.02	< 0.02	0.03	< 0.02
C_3S	62	56	66	64	58	63	59	65
C_2S	16	22	11	11	18	14	18	13
C_3A	11	9	10	10	10	10	8	7
C_4AF	9	10	9	9	9	10	10	10
Free lime	2.46	1.60	3.65	1.45	1.64	1.99	1.40	1.71

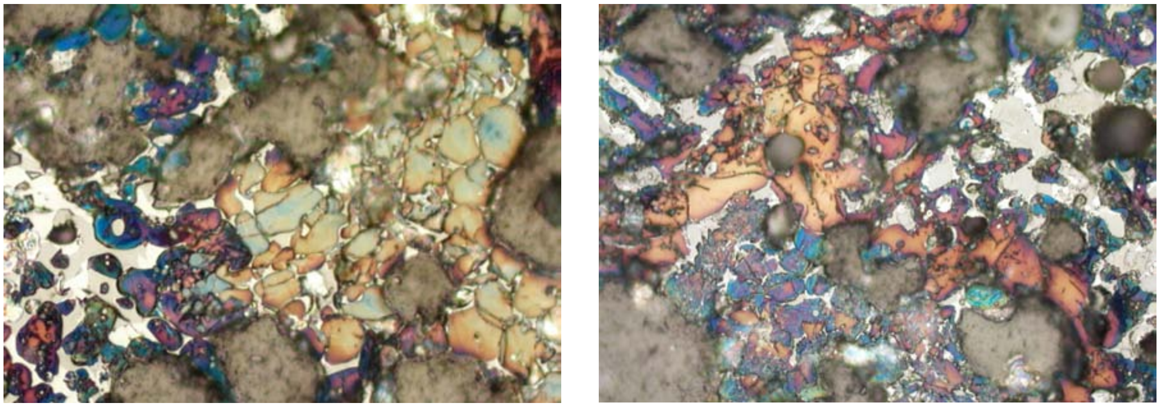
The microscopical examination was conducted on the clinkers to see the distribution and the formation of the major phases, and free lime and/or periclase, if any. The photomicrographs are shown in Figures 8 through 11. The field of view in Figures 8 through 11 is approximately 170 by 240 microns.



Control Mix

Fly ash mix

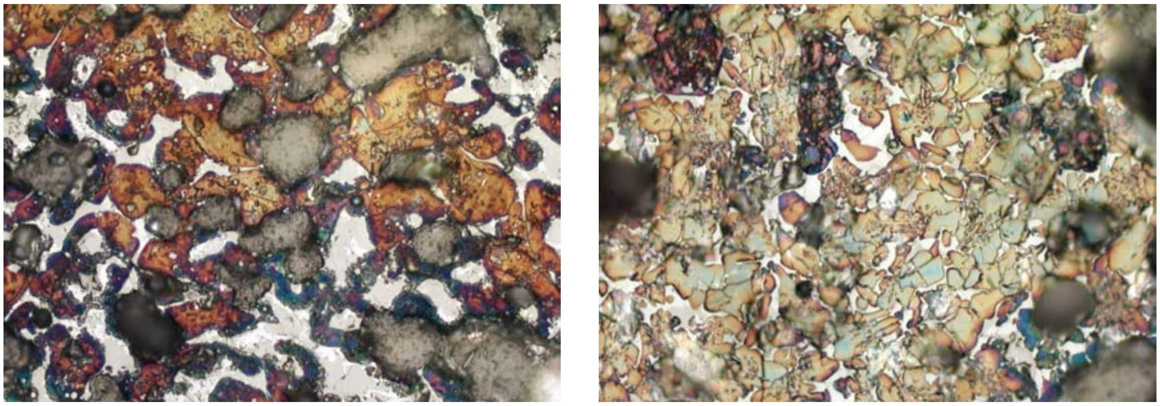
Figure 8. Photomicrographs of Lone Star clinkers showing phase distribution



Control Mix

Fly ash mix

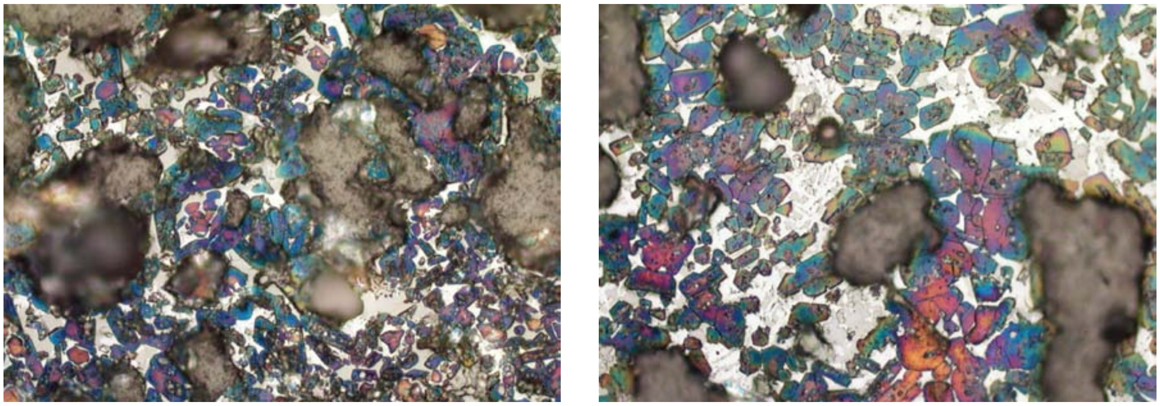
Figure 9. Photomicrographs of Dixon-Marquette clinkers showing phase distribution



Control Mix

Fly ash mix

Figure 10. Photomicrographs of Illinois Cement clinkers showing phase distribution



Control Mix

Fly ash mix

Figure 11. Photomicrographs of Lafarge clinkers showing phase distribution

The microscopical examination confirms all of the major phases, i.e. alite, belite, tricalcium aluminate, and tetracalcium aluminoferrite in all of the clinkers. The aluminate and ferrite phases were observed in the matrix around the alite and belite crystals. In general, little difference were observed between phases formed in the fly ash containing clinkers and the control clinkers. The presence of free lime was observed in the clinkers and their relative amounts were comparable to each other. As expected, due to the pellet size, porosity was relatively high and well distributed. Porosity is a function of the kiln feed pellet size, composition, nodularization, and burning conditions.

Relative grindability of the clinkers was measured by grinding 20 grams of –50/+100 mesh clinker in a small raw mill for a period of 3 hours and measuring the resulting Blaine fineness. Higher finenesses indicate less energy is required to grind the clinkers to a specific fineness. Results are presented in Table 18. Differences in grindability of the fly ash containing and control clinkers are negligible.

Table 18. Blaine fineness (m^2/kg) of the clinkers ground for 3 hours showing the relative grindability

Lone Star		Dixon-Marquette		Illinois Cement		Lafarge	
Control	Fly Ash	Control	Fly Ash	Control	Fly Ash	Control	Fly Ash
360	360	290	260	310	310	270	250

Cement Production and Testing

Cements were produced from all eight clinkers by grinding with the appropriate level of sulfate in a ball mill. Sulfate levels were different for each cement, and were calculated based on the alumina and sulfate contents presented in Table 17. Sulfate was added in the form of gypsum and plaster to simulate the sulfate forms in commercial cement. Cements were ground to an approximate Blaine fineness of 350 m^2/kg. Particle size distribution was measured and is summarized in Table 19. All cements had a wider particle size distribution than that of typical commercial cements.

Table 19. Particle size data of the pilot scale produced cements

Cement Plant	Mix	Retained on a 325 mesh (45 μm) sieve, percent	Mean Diameter, μm
Lone Star	Control	8.6	16.2
	Fly Ash	6.5	14.2
Dixon-Marquette	Control	8.3	15.4
	Fly Ash	6.8	16.7
Illinois Cement	Control	10.8	17.9
	Fly Ash	11.6	15.0
Lafarge	Control	8.2	14.2
	Fly Ash	7.7	14.6

Cements were tested in accordance with ASTM C 150, “Standard Specification for Portland Cement”. This specification sets minimum/maximum chemical and physical standard and optional requirements for five cement types.

Chemical requirements of ASTM C 150 for a Type I Portland cement require a maximum magnesium oxide content of 6.0%, a maximum sulfate content of 3.0 to 3.5% (depending on the C_3A content), a maximum loss on ignition of 3.0%, and a maximum insoluble residue of 0.75%. Optional requirements include a total alkali content (expressed as equivalent Na_2O) of 0.60%. Data presented in Table 20 indicate that all cements meet the standard and optional chemical requirements of a ASTM C 150 Type I Portland cement.

Table 20. Select calculated phases (% wt.) in pilot scale production cements

Analyte	Lone Star		Dixon-Marquette		Illinois Cement		Lafarge	
	Control	Fly Ash	Control	Fly Ash	Control	Fly Ash	Control	Fly Ash
SiO_2	20.74	21.40	20.26	20.00	20.34	20.26	21.16	20.82
Al_2O_3	5.80	5.33	5.31	5.52	5.56	5.68	4.92	4.75
Fe_2O_3	2.80	3.00	2.93	2.91	2.83	2.99	3.24	3.21
CaO	65.73	64.61	64.92	64.39	63.50	64.81	64.43	64.81
MgO	1.90	1.94	3.36	3.91	3.96	2.84	3.01	3.42
SO_3	2.75	2.52	2.52	2.62	2.64	2.69	2.33	2.26
equiv. Na_2O	< 0.02	0.08	< 0.02	0.01	0.02	< 0.02	0.03	< 0.02

Physical requirements and measured data for all cements are presented in Tables 21 through 23.

Results of ASTM C 151 tests for autoclave expansion reflected the anticipated results. Due to the relatively high free lime content of the fly ash-containing and control clinkers, all cements exceeded the ASTM limits. As previously mentioned, this result was expected and is typical of clinkers produced on a pilot scale. This is evidenced by cement produced from kiln feeds supplied by the cement plants, burned in our pilot-scale rotary kiln also exceeding the ASTM limits.

Table 21. ASTM C 109 compressive strength (psi) of pilot scale cements

Cement Plant	**Mix**	**3-day**		**7-day**		**28-day**	
		Actual	***Req'd****	**Actual**	***Req'd****	**Actual**	***Req'd****
Lone Star	Control	3,030	***1,800***	3,550	***2,800***	5,490	***NR****
	Fly Ash	3,040		3,760		5,580	
Dixon-Marquette	Control	3,110		3,990		5,800***	
	Fly Ash	3,300		4,970		6,480	
Illinois Cement	Control	3,340		4,790		6,710	
	Fly Ash	3,620		4,990		6,760	
Lafarge	Control	2,550		3,700		5,490	
	Fly Ash	3,680		5,050		6,660	

* Required minimum compressive strength.
** The minimum 28 day strength is not specified for a Type I cement.
*** 28-day compressive strength was estimated. Specimens were actually tested at an age of 6 days.

Table 22. ASTM C 185 air content of pilot scale cements

Cement Plant	**Mix**	**Air Content, vol.%**	
		Actual	***Requirement****
Lone Star	Control	5.9	***12***
	Fly Ash	5.7	
Dixon-Marquette	Control	5.3	
	Fly Ash	5.4	
Illinois Cement	Control	5.3	
	Fly Ash	5.7	
Lafarge	Control	5.5	
	Fly Ash	4.9	

* The maximum permissible air content.

Table 23. ASTM C 191 time of set of pilot scale cements

Cement Plant	**Mix**	**Time of Set, minutes**		
		Actual	***Requirement****	
			Min.	***Max.***
Lone Star	Control	106	***45***	***375***
	Fly Ash	190		
Dixon-Marquette	Control	95		
	Fly Ash	119		
Illinois Cement	Control	145		
	Fly Ash	160		
Lafarge	Control	140		
	Fly Ash	110		

* The acceptable range of setting time.

Data presented in Tables 21 through 23 indicate that all cements meet the standard physical requirements of an ASTM C 150 Type I Portland cement. As noted in Table 21, compressive strength development of cements produced from fly ash containing clinkers was increased. High early strength and increased ultimate strength are desirable for faster turn-around-time during construction.

Additional testing was performed to assess the potential for early stiffening (ASTM C 359) of the cements. Early stiffening tests indicated that none of the cements except the cement made from Illinois Cement clinker with fly ash showed any tendencies for early stiffening or false setting. The Illinois Cement clinker with fly ash showed moderate tendency for false setting. False setting tendencies are mainly due to the C_3A concentration and reactivity, and are managed by varying the sulfate form (i.e. anhydrite, plaster, or gypsum) present in the cement. Because the aluminate phase concentration is unchanged between the Illinois Cement control and fly ash clinkers, the false setting tendencies are due to the sulfate level or phase that was added to produce the cement.

Alkali-silica reactivity (ASR) testing was not performed because the alkali content of the cements was less than or equal to 0.08%, as shown in Table 20. Simply stated, the alkali-silica reaction is an expansive reaction where the alkalis present in cement react with silicates found in many aggregates. If either the alkalies or reactive silica are not present, the reaction does not occur. Cements made during this project had alkali contents of 0.08% or less. In practice, cements with maximum alkali contents of 0.6% are often used with siliceous aggregates to produce concrete that is free of ASR. Very low alkali contents are expected from pilot-scale kiln-burned clinker due to ease of alkali volatilization. Clinker produced in a commercial kiln would retain higher alkali content.

CONCLUSIONS AND RECOMMENDATIONS

The research and testing performed indicate that high carbon fly ash can conveniently be used in making clinkers that are comparable in characteristics to those prepared from the kiln feeds on both the bench and pilot scales. The fly ash being rich in silica, alumina, and iron oxide, primarily replaces clay, shale, sand, and millscale in the kiln feed. The extent of replacement depends upon the composition of the ash and compatibility with the raw materials of a given cement plant.

The presence of carbon supplements the fuel value to result in significant fuel savings. As noted with the difference in carbon contents of the CWLP fly ashes, the fuel savings are dependent upon the level of carbon present in the fly ash, and the amount of replacement being made. It has also been realized that these high-carbon fly ashes do not release any volatile matters that may cause emission problems during the kiln combustion.

Bench scale testing of seven clinkers (made from three fly ashes and raw materials from four plants) showed clinkers had similar chemical properties with that of the target clinkers prepared directly from the kiln feed from the respective plants.

Pilot-scale production and testing of clinkers from fly ash containing raw feeds and companion kiln feed from the four Illinois cement plants indicated that clinkers had similar chemical properties. Cements made from all clinkers met the standard requirements of ASTM C 150 Type I Portland cement. Cements made from fly ash containing clinkers had improved compressive strength development.

Due to the limitations of the pilot-scale rotary kiln used for clinker production, measurements to document the fuel savings could not be performed and the alkali and sulfate contents of all clinkers were reduced from those expected due to volatilization. Fuel savings with fly ash, although not documented on the pilot-scale, are real and are inferred from the DSC analyses. Calculated fuel savings for the pilot-scale produced cements, if produced at the respective cement plant range from 3.6 to 8.8 percent of the total fuel energy.

Alkalies and sulfates were almost totally removed from all clinkers because CTL's rotary kiln does not utilize exhaust gases for intimate heat exchange to the kiln feed, like commercial cement kilns. Therefore, XRF analyses of fly ash clinkers do not reflect the reduced alkali content of the fly ash raw mixes as compared to the control kiln feeds.

Plant scale testing is the logical next step for proof of concept. Minor material handling problems with the fly ash are anticipated. Planning is already underway for a cement plant scale production of a fly ash containing clinker.

DISCLAIMER STATEMENT

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