ABSTRACT

This report describes the efforts rendered towards the implementation of the high-carbon fly ash technology in the manufacture of portland cement. The program started with the formation of implementation teams and organizing technical meetings to address logistical issues that restricted the implementation of this technology. The efforts culminated into large-scale commercial demonstrations involving cement plants and fly ash producing power stations. Specifically, commercial-scale demonstrations were run at two Illinois cement plants - Illinois Cement and Dixon-Marquette Cement. The plants used large volume of high-carbon fly ash from participating power stations namely Ameren’s Coffeen Power Station and Edwards Power Station. Both the commercial demonstrations realized several material, operational, and environmental benefits.

The data from the Illinois Cement demonstration that used nearly 200 tons of high-carbon fly ash from the Coffeen Power Station, showed a reduction in fuel consumption and NOx emissions, a marginal increase in clinker production, and a significant improvement in cement strength. The demonstration was followed by a number of technical meetings between the partnering teams, CTL, ICCI, and DCEO to resolve issues to pave the way for implementing the high-carbon fly ash technology. Consequently, a proposal by Illinois Cement to modify infrastructure to accommodate fly ash delivery and use on long-term basis was discussed, and is pending decision of development funding by DCEO.

Another large-scale demonstration was carried out at Dixon-Marquette Cement. Over 400 tons of high-carbon fly ash from Ameren’s Edwards Power Station was used as a raw feed component. The high-carbon ash replaced more than half of the clay constituent in the raw mix. The use of fly ash in this demonstration also realized several material, operational, production, and product benefits. The manufacturing operation was efficient, stable, and predictable; the plant showed a substantial increase in production. Clinker also showed significant decrease in alkalies and sulfate contents. This was a product improvement without process or equipment modifications. Cement exhibited strength properties far exceeding the required standard specifications.
EXECUTIVE SUMMARY

The objective of the project was to commercially demonstrate the use of high-carbon Illinois coal fly ash as a raw feed component and a fuel supplement in the manufacture of portland cement, and subsequently implement the technology at Illinois cement plants.

In order to achieve this objective, the project started with the formation and finalization of three implementation teams 1) Ameren, Illinois Cement, and CTL, 2) Dynergy, Dixon-Marquette Cement, and CTL; and 3) Dairyland Power, Holcim Cement, and CTL. This was followed by technical meetings between the teams to address critical issues hindering the implementation of the fly ash technology. As a result of the meetings and the degree of interest shown by team members, only the two most interested teams emerged; they were Ameren, Illinois Cement, and CTL, and 2) Ameren, Dixon-Marquette Cement, and CTL. Further meetings between these teams culminated into large-scale commercial demonstrations as a step towards the full-scale implementation of technology.

Two large-scale commercial demonstrations were conducted. These demonstrations involved the participation of 1) Illinois Cement, located in LaSalle, using high-carbon fly ash from Ameren’s Coffeen Power Station, located in Coffeen; and 2) Dixon-Marquette Cement, located in Dixon, using high-carbon fly ash from Ameren’s Edwards Power Station, located in Peoria.

Both the Coffeen and Edwards Power Stations use Illinois coal and produce high-carbon fly ash that is available in a dry form.

Approximately 200 tons of high-carbon fly ash was transported by pneumatic trucks from Ameren’s Coffeen Power Station to Illinois Cement and blended at a rate of 3.5% with the other raw materials. The demonstration lasted for nearly 3 days and realized several benefits. The kiln operated in an efficient, stable, and predictable manner. As a result, the cement plant realized fuel savings, a reduction in NOx emissions, a marginal increase in clinker production, and a significant improvement in cement compressive strength. The final report on the demonstration has already been submitted to ICCI.

This successful demonstration of the technology was followed up by a series of technical meetings between Illinois Cement and Ameren’s Coffeen Power Station as the partnering teams, CTL as the technology developer, and ICCI as the technology promoter. The meetings were aimed at identifying and resolving any logistical issues to facilitate the implementation of technology. Consequently a proposal by Illinois Cement was developed and presented to the ICCI proposing modification of infrastructure at the plant to accommodate fly ash delivery and its use on long-term basis. The proposal also included cost estimates for acquiring the necessary infrastructure. The proposal is with ICCI for further study and discussion with Department of Commerce and Economic Opportunity (DCEO) on possible funding.

The second large-scale demonstration was carried out at Dixon-Marquette Cement. The demonstration used 420 tons of high-carbon fly ash from Ameren’s Edwards Power Station. The ash was blended with the raw mix at a rate of 4.5% that replaced nearly
60% of the clay constituent in the raw mix. The demonstration lasted for over 4 days and realized several material, operational, production, and product benefits. The Dixon-Marquette plant has three short preheater kilns and one long dry kiln. It was noticed that during the demonstration, the manufacturing operation was normal, efficient, stable, and predictable. Although all four kilns were included in the demonstration, only two of the kilns were monitored during the demonstration. The incorporation of the high-carbon fly ash resulted in an increase in production, especially with the short kiln, where a production increase of 10% was recorded. Clinker from the long kiln showed significant decrease in alkalies and sulfate contents; this is a critical product improvement without process or equipment modifications. The clinker exhibited properties comparable or better than the normally produced clinker. Cement exhibited strength properties far exceeding the required standard specifications.

Following the successful demonstration of the fly ash technology, CTL is in pursuance with Dixon-Marquette Cement to the implementation of this technology. A series of technical meetings between Dixon-Marquette, Ameren’s Edwards Power Station, CTL, ICCI, and DCEO personnel are being planned to address and resolve logistical issues, if any, and to pave the way for implementation of this technology on long-term basis.

CTL, being the technology developer, plans to continue providing necessary onsite and offsite technical assistance to ensure that the technology is successfully implemented, and does not falter for lack of technical assistance or any other unforeseen reasons.
OBJECTIVES

The objectives of the project are to demonstrate the commercial feasibility of using high-carbon fly ash from Illinois coal in the manufacture of portland cement, and subsequently to implement the technology at the participating Illinois cement plants. To be successful, this technology needs participation and partnering of a cement plant and a power plant that produces high-carbon fly ash. The strongest partnerships are 1) Illinois Cement in LaSalle, using high-carbon fly ash from Ameren’s Coffeen Power Station in Coffeen, and 2) Dixon-Marquette Cement in Dixon, using high-carbon fly ash from Ameren’s Edwards Power Station in Peoria.

The implementation of fly ash technology will provide two major benefits to cement manufacturing. First, the fly ash would partially replace raw materials such as shale and clay which are normally mined or purchased. Second, the carbon content of the fly ash will provide a fuel supplement for the energy intensive manufacturing process.

Additionally, based on the results of CTL’s previous ICCI-sponsored projects, and several assumptions, the implementation of high-carbon fly ash technology may make the following interrelated material, operational, product, and environmental objectives plausible:

1. The cement plant should be able to conserve at least 50,000 Btu/ton of clinker because of the energy value (carbon content) of the ash.
2. The cement plant should be able to realize at least a 1% increase in production capacity of the kiln.
3. The quality of the cement, as judged by the ASTM C 150 specifications, should be fully comparable with that produced using the original raw materials.
4. There is every likelihood that the cement produced by using fly ash would have reduced-alkali contents, primarily because the fly ash contain lower alkalis than the clay and shale they replace. Low-alkali cements are in high demand for their diminished alkali-silica reactivity.
5. Use of fly ash will also result in low-alkali cement kiln dust (CKD), which is easily recyclable, as compared to the high alkali cement kiln dust that the plant often must discard.
6. The power stations should realize economics of this technology that are favorable relative to the other competitive strategies.

INTRODUCTION AND BACKGROUND

Over 3 million tons of fly ash is annually generated in Illinois; less than two-third of this ash is used in commercial products. The remainder is landfilled. The continued implementation of the environmental policies to reduce NOx emissions at coal-fired power plants, will further increase the production of fly ash with significantly high L.O.I.s (loss on ignition) and unburned carbon contents. In typical cement manufacturing silica, alumina, and iron contents are necessary in the raw mix. Since fly ash is rich in these compounds, it can be conveniently used in the formulation of cement raw feed, whereas the unburned carbon in the fly ash would contribute to fuel saving in the energy intensive cement manufacturing process.
This report entails the use of high-carbon fly ash technology on commercial scale and discusses its implementation at cement plants. As mentioned earlier, the project started with the formation of three implementation teams 1) Ameren Energy, Illinois Cement, and CTL; 2) Dynergy, Dixon-Marquette Cement, and CTL; and 3) Dairyland Power, Holcim Cement, and CTL. However, during the team meetings to address the critical issues for the implementation of technology, and the degree of interest shown by the members, only the two most interested teams emerged. These were Ameren and Illinois Cement; and Ameren and Dixon-Marquette Cement. As a result, two commercial-scale demonstrations took place at these cement plants using fly ash from the respective power stations that brought the project a step closer to the implementation stage.

During these demonstrations, large quantities of high-carbon fly ash from Ameren’s Power Stations at Coffeen and Edwards were respectively utilized at Illinois Cement and Dixon-Marquette Cement plants. The fly ash was blended with the cement plant raw mix, fired into cement clinker, and then ground into Portland cement. Cement and clinker samples were characterized and compared to those normally produced at the plant. During the demonstrations, the operation, processing, and material benefits resulting from the use of high-carbon fly ash were documented.

The final report on the demonstration at Illinois Cement using Coffeen’s high-carbon fly ash has already been submitted to the ICCI. However, a summary of the findings is included in the report. The demonstration at Dixon-Marquette using Edwards fly ash is described below.

In order to implement the technology at the cement plants, a number of subsequent meetings were organized and more are being organized to address critical implementation issues. A number of such meetings involved key personnel from Illinois Cement, Ameren, CTL, ICCI, and DCEO who discussed logistical issues including possible process and infrastructure modifications that may be required for successful implementation of this technology.

RESULTS AND DISCUSSION

Phase I
Task 1. Finalization of Implementation Teams
The project started with the formation and finalization of three potential implementation teams of - 1) Ameren, Illinois Cement, and CTL, 2) Dynergy, Dixon-Marquette Cement, and CTL; and 3) Dairyland Power, Holcim Cement, and CTL. The teams were composed of one cement manufacturer and one fly ash producer, whereas CTL was the technology developer.

Task 2. Team Meetings
As the technology developer, CTL organized a series of team meetings to discuss and resolve critical issues in order to facilitate the implementing of fly ash technology at the participating cement plants. The meetings frequently took place at CTL, cement plants, and power stations, as deemed appropriate.
Task 3. Addressing the Issues
The team members vigorously discussed the logistics, economy, and material issues pertaining to the availability and uniformity of fly ash. Also discussed were the fly ash and cement raw material compatibility along with the plant-specific concerns in order to arrive at a reasonable understanding on the implementation issues. Based on the discussions and level of interest expressed at the meetings, the following two teams remained as the most interested parties towards the implementation phase.

1) Ameren, Illinois Cement, and CTL
2) Ameren, Dixon-Marquette Cement, and CTL

Phase II
After further discussion, the two teams proceeded to perform large-scale demonstrations at the cement plants.

Tasks 4, 5, and 6. Preparation for Trial Burns, Onsite and Offsite Trial Burn and Related Technical Support
Two large-scale demonstrations were carried out at the cement plants using high-carbon fly ashes from the respective power stations; the participating plants were:

- Ameren’s Coffeen Power Station (Coffeen) and Illinois Cement (LaSalle)
- Ameren’s Edwards Power Station (Peoria) and Dixon-Marquette Cement (Dixon)

Details of the demonstration and the subsequent technical meetings to discuss implementations of the technology are given in the following sections.

DEMONSTRATION AT ILLINOIS CEMENT PLANT

Nearly 200 tons of high-carbon fly ash from the Coffeen Power Station was blended at a 3.5% addition rate with the raw mix at Illinois Cement, which is a dry process plant with multistage cyclone preheaters (Figure 1). The demonstration was carried out for a period of nearly 3 days and realized several operational, product, and environmental benefits.

![Figure 1. Illinois Cement with a clinker capacity of 1700 ton/day](image)
As mentioned earlier, the final report on this demonstration has already been submitted to ICCI; a summary of the demonstration is as follows.

**Fly Ash Characterization**
Prior to the demonstration, the fly ash was analyzed for its composition and compatibility with cement raw mix. The composition of ash is shown in Table 1, which also shows a 12.97% loss of ignition that is largely attributable to unburned carbon.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Wt., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>47.87</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17.08</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.59</td>
</tr>
<tr>
<td>CaO</td>
<td>4.68</td>
</tr>
<tr>
<td>MgO</td>
<td>1.21</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.21</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.02</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.77</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.13</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The ash was also analyzed by differential scanning calorimetry (DSC) to determine its fuel content and the presence of any organic volatile species which may cause emission-related issues. The DSC plot for the ash is shown in Figure 2.

A large exothermic peak at temperatures above 450°C in the DSC plot 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 matters in the ash.
Also of interest in the plot is the presence of an endotherm below 450°C. This property of the fly ash tends to contribute to a temperature reduction in the upper preheaters leading to clearer pathways and smoother material flow.

**Raw Mix Formulation**
The analyses of the cement kiln feeds without and with the anticipated fly ash addition (3%) prior to the demonstration is shown in Table 2. The composition of the raw feed during demonstration was close to that shown in the right most column of Table 2.

**Table 2.** Composition of cement kiln feed with and without fly ash addition

<table>
<thead>
<tr>
<th>Analyte (on ignited basis)</th>
<th>Kiln feed</th>
<th>Kiln feed + 3% fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.50</td>
<td>22.37</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.40</td>
<td>6.64</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.32</td>
<td>2.84</td>
</tr>
<tr>
<td>CaO</td>
<td>66.67</td>
<td>61.90</td>
</tr>
<tr>
<td>MgO</td>
<td>3.25</td>
<td>3.06</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.94</td>
<td>0.91</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.30</td>
<td>0.44</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.04</td>
<td>1.30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.28</td>
<td>0.37</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.12</td>
<td>0.13</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.21</td>
<td>0.20</td>
</tr>
<tr>
<td>Total</td>
<td>100.16</td>
<td>100.28</td>
</tr>
</tbody>
</table>

**Clinker Characterization**
The clinkers produced before and during the demonstration were collected and tested for oxide analyses and Bogue composition (Table 3a, b).

**Table 3a.** Clinker composition (wt. %) before and during the demonstration

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Before</th>
<th>During</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21.04</td>
<td>21.06</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.89</td>
<td>5.90</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.46</td>
<td>2.55</td>
</tr>
<tr>
<td>CaO</td>
<td>63.79</td>
<td>63.32</td>
</tr>
<tr>
<td>MgO</td>
<td>2.42</td>
<td>2.92</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.95</td>
<td>1.79</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.45</td>
<td>0.46</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.19</td>
<td>1.19</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Loss on Ignition (L.O.I)</td>
<td>0.22</td>
<td>0.18</td>
</tr>
</tbody>
</table>
Table 3b. Bogue composition clinkers before and during the demonstration

<table>
<thead>
<tr>
<th>Calculated Bogue compounds, wt. %</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>C₂S</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>C₃A</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>C₄AF</td>
<td>7</td>
<td>8</td>
</tr>
</tbody>
</table>

The data from Bogue composition and the subsequent XRD analysis (Figure 3) confirmed the presence of major C₃S, C₂S, C₃A, and C₄AF phases in the clinkers.

Figure 3. XRD Patterns of clinker produced during the demonstration

An absence of free lime peak in the demonstration clinkers (composite #2 and #3) as compared to the one produced without fly ash (composite #1) is noteworthy. This can be attributed to improved reactivity of lime in the raw mix with fly ash.

The photomicrographs of the clinkers produced before and during the demonstration are shown in Figure 4.

Figure 4. 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 (C₃S), and the round crystals with lamellae are belites (C₂S). The interstices are composed of tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF), also known as the melt phases.

As can be seen in clinkers produced before the demonstration (Figure 4a), 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 4b), 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 specifications. The results are shown in Table 4. Data on cements produced prior to the demonstration are also shown for comparison.

**Table 4. ASTM C 150 data of cements**

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>During</th>
<th>ASTM limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM C 204 - Fineness, air permeability (Blaine), m²/kg</td>
<td>375</td>
<td>372</td>
<td>280 (min)</td>
</tr>
<tr>
<td>ASTM C 109 - Compressive strength, psi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-day</td>
<td>3130</td>
<td>3490</td>
<td>1800 (min)</td>
</tr>
<tr>
<td>7-day</td>
<td>4070</td>
<td>4250</td>
<td>2800 (min)</td>
</tr>
<tr>
<td>28-day</td>
<td>5020</td>
<td>5290</td>
<td>4060</td>
</tr>
<tr>
<td>ASTM C 191 – Vicat time of set, minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>135</td>
<td>120</td>
<td>45 (min)</td>
</tr>
<tr>
<td>Final</td>
<td>160</td>
<td>140</td>
<td>375 (max)</td>
</tr>
<tr>
<td>ASTM C 185 – Air content, %</td>
<td>7.2</td>
<td>7.1</td>
<td>12 (max)</td>
</tr>
<tr>
<td>ASTM C 151 – Autoclave expansion, %</td>
<td>0.34</td>
<td>0.11</td>
<td>0.80 (max)</td>
</tr>
</tbody>
</table>

It is evident from the data that the cement produced during demonstration complied with all requirements established by ASTM C 150 specification. 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$_2$O). In addition, the total gas flow, temperature, and pressure were recorded. Results are summarized in Table 5.

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 5. Data on stack emissions before, during, and after the demonstration at Illinois Cement**

<table>
<thead>
<tr>
<th>Emissions</th>
<th>Before</th>
<th>During</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO, lb/hr</td>
<td>209</td>
<td>200</td>
<td>273</td>
</tr>
<tr>
<td>NO, lb/ton clinker</td>
<td>2.65</td>
<td>2.53</td>
<td>3.56</td>
</tr>
<tr>
<td>CO, lb/hr</td>
<td>95.3</td>
<td>276</td>
<td>158</td>
</tr>
<tr>
<td>CO, lb/ton clinker</td>
<td>1.21</td>
<td>3.60</td>
<td>1.99</td>
</tr>
<tr>
<td>CO$_2$, %</td>
<td>15.2</td>
<td>16.6</td>
<td>16</td>
</tr>
<tr>
<td>H$_2$O, %</td>
<td>9.1</td>
<td>9.1</td>
<td>9.2</td>
</tr>
<tr>
<td>SO$_2$, ppm</td>
<td>11.6</td>
<td>47.0</td>
<td>25.8</td>
</tr>
<tr>
<td>O$_2$, % dry</td>
<td>11.7</td>
<td>11.2</td>
<td>11.2</td>
</tr>
<tr>
<td>Flow, Wet SCFM</td>
<td>156092</td>
<td>156092</td>
<td>156092</td>
</tr>
</tbody>
</table>

**Critical Operational Observations**

Some selected critical observations and benefits, however, are summarized here:

- Operation ran smooth and normal, no undue effects to operation caused by the incorporation of high-carbon fly ash
- Emissions of oxides of nitrogen (NO$_x$) reduced
- Fuel consumption reduced by 2.6%
- Clinker production marginally increased

**Follow-up Implementation Meeting Between Partnering Teams**

Following the successful large-scale demonstration, technical meetings between Illinois Cement, Ameren, CTL, ICCI, and DCEO were organized to further the implementing of high-carbon fly ash technology at Illinois Cement. The discussion centered on the logistics and infrastructure options available for the implementation of technology. Illinois Cement internally studied the costs related to the implementation of technology and the acquisition of infrastructure modifications. Illinois Cement developed a cost proposal for these modifications and submitted to the ICCI for possible funding.
A large-scale commercial run was conducted at Dixon-Marquette Cement plant using high-carbon fly ash from Ameren’s Edwards Power Station. Nearly 420 tons of fly ash were used in the demonstration that was carried out for over 4 days.

Fly Ash Characterization
Prior to the demonstration, high-carbon fly ash from Edwards Power Station was characterized for its chemical constituents. The fly ash was also evaluated for its compatibility with the cement plant raw mix in order to formulate a mix design compatible with the target raw feed.

Chemical Composition. The chemical analysis of the fly ash was determined by the X-ray fluorescence (XRF) method; the data is shown in Table 6.

Table 6. Oxide composition of the Edwards fly ash

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Wt., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>21.62</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>8.53</td>
</tr>
<tr>
<td>CaO</td>
<td>3.80</td>
</tr>
<tr>
<td>MgO</td>
<td>1.09</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.48</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.15</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.06</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.03</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.40</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>0.04</td>
</tr>
<tr>
<td>Loss on Ignition (L.O.I)</td>
<td>6.91</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>99.62</strong></td>
</tr>
</tbody>
</table>

Based on the oxide analysis the ash is classified as ASTM C 618 Class F fly ash. The L.O.I. of 6.91% is largely attributed to the unburned carbon in the ash that can potentially result in significant fuel value. The fly ash was a finely divided free-flowing dry material with 80% grain size being less than No. 200 mesh.

Thermal Behavior and Fuel Value of the Fly Ash. Using differential scanning calorimetry (DSC), the fly ash was evaluated for its fuel value and for the presence of any volatiles and other organic compounds together with their temperatures of release. DSC plot of the ash is shown in Figure 5.
Similar to the Coffeen fly ash, the lack of any exothermic peak at temperatures below 450°C suggests absence of volatile matters in the fly ash. This essentially means that the ash will not generate any organic volatile in the upper preheater stages of the cement plant. A large exothermic peak at temperatures above 450°C confirms the presence of substantial heat content in the ash. Also of interest in the DSC plot is the presence of endothermic 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 leading to clearer pathways and smoother material flow.

**Raw Feed Formulation**

The commonly employed raw feed at Dixon Marquette Cement is composed of the following raw materials (Table 7).

<table>
<thead>
<tr>
<th>Component</th>
<th>Without fly ash, wt. %</th>
<th>With fly ash, wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>89</td>
<td>89</td>
</tr>
<tr>
<td>Clay</td>
<td>8</td>
<td>3.5</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>-</td>
<td>4.5</td>
</tr>
<tr>
<td>Foundry Sand</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>BOF (basic oxygen furnace) dust</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Edwards fly ash was used at 4.5% addition, replacing nearly 60% of the clay. The composition of the raw feed is critical in order to prepare a replicate raw feed when using the high-carbon fly ash as a component material. The composition of the feed after fly ash addition is presented in Table 8.
Table 8. Raw feed composition with high-carbon fly ash

<table>
<thead>
<tr>
<th>Analyte (ignited basis)</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.41</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.95</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.41</td>
</tr>
<tr>
<td>CaO</td>
<td>63.77</td>
</tr>
<tr>
<td>MgO</td>
<td>3.36</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.96</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.17</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.74</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.24</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.06</td>
</tr>
<tr>
<td>Total</td>
<td>99.27</td>
</tr>
</tbody>
</table>

Fly Ash Collection, Transportation, and Processing

Nearly 420 tons of high-carbon fly ash was collected dry from the Edwards Power Station and transported to Dixon Marquette Cement using pneumatic loading transport trucks. Figure 6 shows a transport truck during unloading of the fly ash at Dixon-Marquette. The fly ash was pneumatically offloaded at the cement plant into a portable silo before leading to the raw material stream through a weighfeeder. Being dry and free flowing material the fly ash offloading was extremely smooth.

Figure 6. Fly ash transport truck and pneumatic unloading into a portable silo at Dixon Marquette Cement

The ash was blended with the raw materials used at the cement plant i.e., crushed limestone with a small amount of clay and sand, ground into raw feed. Again, being dry and a finely divided free flowing material, the blending of fly ash with other raw materials was easy and required no pre-processing.
Kiln Operation
Dixon-Marquette is a dry operation with four kilns – three short kilns with preheaters and one long kiln (Figure 7). The raw feed is prepared by two raw mills and blended as one feed and fed to all four kilns. Fly ash was introduced into one raw mill and blended with the feed from the other mill into a common silo. The feed was introduced into the top stage of the preheaters (stage 1) of the multi-stage preheaters for the three short kilns (Kiln #1, #2, and #3); and to the entrance of the long kiln (Kiln #4) simultaneously.

![Image of kilns with preheaters and a long kiln](image)

**Figure 7. Three short kilns with preheaters (left) and one long dry kiln (right) at Dixon Marquette Cement**

For the preheater kilns, the raw feed travels through different stages and is preheated prior to entering into the rotary kiln. The raw feed moves from one preheater stage to the next counter current to the flow of the incoming hot flue gases from the kiln. A noticeable degree of calcination of the raw feed occurs by the time the feed left the final stage (fourth stage) of the preheaters.

Parameters Observed
Several key parameters were observed while the kiln operation was in progress. Particular attention was given to operational parameters related to carbon containing fly ash benefiting the overall operation as compared to those prior to the demonstration.

Although, at the Dixon-Marquette Cement plant there were three short kilns and one long kiln, the observation of parameters are reported only on one short kiln (Kiln #1) and the long kiln (Kiln #4) as follows:

**Production Rate.** During the demonstration, a noticeable increase (10%) in clinker production of Kiln #1 was observed. The production increased from 400 tons/day to nearly 440 tons/day for Kiln #1 (Figure 7); the production rate returned to the pre-demonstration level after the demonstration.
The increase in production can be attributed to both 1) carbon in the fly ash which had caused an increased calcination of the raw feed prior to entry into the kiln, and 2) improved reaction due to reactive nature of the finely divided fly ash particles with lime (CaO) from limestone. In case of the Kiln #4, although such significant production increase was not observed, the kiln did run smoothly and exhibited marginal production increase.

**Burning Zone Temperature.** Although no change in temperature was made to accommodate the contribution of carbon from the fly ash, the morphology of belite crystals in clinker from short kiln (Kiln #1) during the demonstration (amoeboidal crystals instead of typical round belite in the photomicrographs, see Figure 8, left) suggested their formation at high temperature. This high temperature clinker formation may be attributed to the residual carbon incorporated into the kiln feed (through fly ash) that managed to pass through the preheaters into the kiln burning zone.
Figure 9. Photomicrographs of demonstration clinkers from Kiln #4 (long kiln) with fly ash (left) and without fly ash (right)

Photomicrographs of clinkers produced in long kiln (Kiln #4) are also shown in Figure 9 for comparison. It must be mentioned that in case of the long kiln there was no abnormal temperatures recorded in the chain section of the kiln because of the high-carbon in fly ash. The kiln did run extremely well without any abnormal temperature variations during the entire demonstration.

**Fuel Consumption/Fuel Rate.** As mentioned above, the temperature of the burning zone was not adjusted during the demonstration. However, had the temperature been adjusted to its normal operational level, noticeable fuel savings resulting from the high-carbon fly ash in the kiln feed could have been realized. According to the data, an addition of 4.5% fly ash having an L.O.I. of nearly 7% would result in nearly 3% fuel savings. A rough estimation of fuel saving from a high-carbon fly ash use can be made as follows:

\[
\text{Fuel savings per ton of clinker (\%) } = \frac{\text{L.O.I.} \times \text{addition rate, \%}}{10} \tag{1}
\]

**Example:**

Edwards fly ash with 7% L.O.I. and a use rate of 4.5%, gives;

\[
\text{Fuel savings } = \frac{7 \times 4.5}{10} = 3\%
\]

**General Operational Observations**
During the demonstration of using high-carbon fly ash at Dixon-Marquette, all kilns ran extremely well. There were no problems of material delivery and blending, blocking or plugging of preheaters, abnormal temperature profiles of the preheaters or the kiln. No formation of ‘snowman’ in the cooler was experienced. There were no environmental problems with respect to stack opacity, or detached plumes. From the material standpoint, the demonstration was successful, as the production significantly increased and fuel economy could also be improved.

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* In cement manufacturing parlance, a “snowman” is an agglomeration of fine clinker particles, held together either by a solidified melt phase (clinker melt or salt melt) or electrostatic charge.
Cement Production
The demonstration clinker was blended with an appropriate amount of gypsum and ground into portland cement in a closed-circuit mill at the cement plant. Separately, clinker was characterized for its chemical and mineralogical composition while cement was tested and evaluated for compliance with the ASTM C150 Specifications.

Clinker Characterization
Clinkers produced by the use of high-carbon fly ash during the demonstration were analyzed by XRF. Their phase composition was studied by optical microscopy and XRD.

Oxide Composition. The oxide analysis (see Table 9) shows lower sulfate and lower alkalies in the demonstration clinker produced by using high-carbon fly ash. The lower sulfate and alkalies contents indicate product improvements resulting from the use of the high-carbon fly ash. Low alkalie low sulfate clinkers produce low alkali low sulfate cements that are preferred in concrete for better durability properties. The Bogue compositions of the clinkers (also shown in Table 9) do confirm the presence and appropriate distribution of the major phases C₃S, C₂S, C₃A, and C₄AF.

Table 9. Oxide composition of clinkers

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Kiln #1 with fly ash</th>
<th>Kiln #1 with no fly ash</th>
<th>Kiln #4 with fly ash</th>
<th>Kiln #4 with no fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.93</td>
<td>21.01</td>
<td>20.94</td>
<td>19.83</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.33</td>
<td>5.38</td>
<td>4.86</td>
<td>4.91</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.50</td>
<td>3.39</td>
<td>3.47</td>
<td>3.40</td>
</tr>
<tr>
<td>CaO</td>
<td>62.61</td>
<td>63.34</td>
<td>62.61</td>
<td>61.63</td>
</tr>
<tr>
<td>MgO</td>
<td>3.59</td>
<td>3.41</td>
<td>3.63</td>
<td>3.37</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.83</td>
<td>1.10</td>
<td>1.81</td>
<td>3.36</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.20</td>
<td>0.17</td>
<td>0.19</td>
</tr>
<tr>
<td>K₂O</td>
<td>1.65</td>
<td>1.44</td>
<td>1.75</td>
<td>2.70</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>0.93</td>
<td>0.24</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Alkalies as Na₂O</td>
<td>1.29</td>
<td>1.15</td>
<td>1.33</td>
<td>1.97</td>
</tr>
</tbody>
</table>

Calculated Bogue compounds, wt. %

<table>
<thead>
<tr>
<th>C₃S</th>
<th>59</th>
<th>56</th>
<th>57</th>
<th>61</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂S</td>
<td>13</td>
<td>18</td>
<td>17</td>
<td>11</td>
</tr>
<tr>
<td>C₃A</td>
<td>8</td>
<td>9</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>C₄AF</td>
<td>11</td>
<td>10</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>

Microscopical Analysis. Microscopical examination of the demonstration clinker confirmed a typical distribution and the formation of the major clinker phases as already shown in Figure 8. The presence of amoeboideal belite crystals in clinker with fly ash (instead of typical round belite without fly ash) from Kiln #1 during the demonstration suggests its formation at high temperature. Typically alite are large angular crystals, and belite are smaller round crystals, the interstices are aluminates and ferrite phases. Large dark spot are the pores. An abundance of porosity often makes clinker easy to grind.
**X-Ray Diffraction Analyses.** Comparison of XRD patterns of clinker made during the demonstration (Figure 10) also confirms the presence of major C₃S, C₂S, C₃A, and C₄AF phases. Absence of a free lime peak in the demonstration clinkers from Kiln #1 and Kiln #4 (as compared to the ones produced without fly ash) can be attributed to an improved reactivity lime in the raw mix with fly ash rendered by its fine and glassy particles.

![Figure 10. XRD Patterns of clinker produced during the demonstration](image)

**Cement Testing and Evaluation**
Cement from the clinker produced before and during demonstration was tested for compliance with ASTM C 150, “Standard Specification for Portland Cement”. Results are shown in Table 10.

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>During</th>
<th>ASTM limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM C 185 – Air content, %</td>
<td>6.5</td>
<td>7.5</td>
<td>12 (max)</td>
</tr>
<tr>
<td>ASTM C 204 - Fineness, air permeability (Blaine), m²/kg</td>
<td>378</td>
<td>362</td>
<td>280 (min)</td>
</tr>
<tr>
<td>ASTM C 109 - Compressive strength, psi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-day</td>
<td>4270</td>
<td>3540</td>
<td>1800 (min)</td>
</tr>
<tr>
<td>7-day</td>
<td>5060</td>
<td>4390</td>
<td>2800 (min)</td>
</tr>
<tr>
<td>28-day</td>
<td>-</td>
<td>5460</td>
<td>4060</td>
</tr>
<tr>
<td>ASTM C 191 – Vicat time of set, minutes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>110</td>
<td>110</td>
<td>45 (min)</td>
</tr>
<tr>
<td>Final</td>
<td>250</td>
<td>255</td>
<td>375 (max)</td>
</tr>
<tr>
<td>ASTM C 151 – Autoclave expansion, %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.13</td>
<td>– 0.05</td>
<td>0.80 (max)</td>
</tr>
</tbody>
</table>

The results clearly show that the properties of the cement produced during demonstration are comparable to those of the normally produced cement and are in compliance with the standard specifications.
Follow-up Implementation Meeting Between Partnering Teams

Following the successful large-scale demonstration, technical meetings between Dixon-Marquette Cement, Edwards Power Station, CTL, and ICCI (and DCEO) personnel are being organized in the near future to further the implementing of high-carbon fly ash technology at Dixon-Marquette Cement. The meetings will discuss the logistics and infrastructure options available for the implementation of this technology. Like Illinois Cement, Dixon-Marquette may internally study the costs related to the implementation of technology and the acquisition of the required infrastructure.

Phase III

Tasks 7 and 8. Post-trial Onsite and Offsite Support

CTL, being the technology developer, has continuously been assisting both the cement plants and the power stations with the ongoing technical support. This has been in the form of troubleshooting at the plants (onsite) as well as the laboratory characterization of material (offsite) such as raw materials from cement plants and fly ash from the participating power stations. Fly ash samples from both Coffeen and Edwards Power Stations were tested for the loss on ignition (L.O.I.) as an indication of fuel content. This was aimed at providing a database on the fuel variation of the high-carbon fly ash for eventual use at cement plants. The L.O.I. data on ashes is given in Table 11.

Table 11. Loss on ignition of fly ashes from Coffeen and Edwards Stations in 2003

<table>
<thead>
<tr>
<th>Date of Fly Ash Collection</th>
<th>L.O.I., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coffeen Power Station</td>
<td></td>
</tr>
<tr>
<td>June 13 – 18</td>
<td>19.69</td>
</tr>
<tr>
<td>June 13 – 25</td>
<td>14.87</td>
</tr>
<tr>
<td>June 27 – July 4</td>
<td>13.70</td>
</tr>
<tr>
<td>July 7 – 16</td>
<td>14.23</td>
</tr>
<tr>
<td>July 18 – 30</td>
<td>12.19</td>
</tr>
<tr>
<td>August 1 – 11</td>
<td>13.92</td>
</tr>
<tr>
<td>August 13 – 22</td>
<td>12.63</td>
</tr>
<tr>
<td>August 25 – September, 5</td>
<td>13.63</td>
</tr>
<tr>
<td>September 8 – 15</td>
<td>15.29</td>
</tr>
<tr>
<td>Average</td>
<td>14.46</td>
</tr>
<tr>
<td>Range</td>
<td>12.19 – 19.69</td>
</tr>
</tbody>
</table>

| Edwards Power Station           |          |
| June 6                          | 4.26     |
| June 26                         | 3.96     |
| July 8 (unit #1)                | 7.8      |
| July 8 (unit #2)                | 3.92     |
| July 25 (unit #5)               | 8.60     |
| July 25 (unit #7)               | 5.79     |
| August 8                        | 6.91     |
| Average                         | 5.89     |
| Range                           | 3.96 – 8.60 |
Coffeen Station fly ash has a L.O.I. range of 12.19% – 19.69% with an average of 14.46%. This is as compared to L.O.I. range of 3.96% – 8.60% with an average of 5.89% for Edwards Station fly ash.

Additionally, CTL as the principal developer of the high-carbon fly ash technology, will continue to provide necessary technical assistance to both cement plants and the power stations to ensure that once the technology is implemented, it remains in place and does not falter due to lack of technical support.

CONCLUSIONS AND RECOMMENDATIONS

The commercial-scale demonstrations at two separate cement plants using separate fly ashes have shown that cement manufacturing can be employed as a large volume consumer of high-carbon fly ash produced in Illinois. The commercial demonstrations points to the emergence of a new market for non-usable high-carbon fly ashes with tangible material, operational, product, and environmental benefits to both the power plants and cement industry.

Following the successful demonstration on the fly ash technology, the logistics for implementing the technology are being vigorously addressed in joint technical meetings between the key personnel from the cement plants, the partnering fly ash producers, CTL, and ICCI. The meetings are being organized to particularly resolve material, operational, and plant-specific issues. As requested, CTL will assist the cement plants and power stations in proposing to ICCI and DCEO for any funding necessary infrastructure modifications for long-term implementation of the technology. CTL, being the technology developer, also plans to continue providing necessary onsite and offsite technical assistance to ensure that the technology is successfully implemented and does not falter due to lack of technical support.

ACKNOWLEDGEMENTS

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This report was prepared by Javed I. Bhatt y, Ph.D., ICCI Principal Investigator, and Construction Technology Laboratories, Inc. (CTL) with support, in part by grants made possible by the Illinois Department of Commerce and Economic Opportunity through the Office of Coal Development and the Illinois Clean Coal Institute. Neither Dr. Bhatt y and Construction Technology Laboratories, Inc. (CTL) nor any of its subcontractors nor the Illinois Department of Commerce and Economic Opportunity, Office of Coal Development, Illinois Clean Coal Institute, nor any person acting on behalf of either:

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