FINAL TECHNICAL REPORT
September 1, 2003, through July 31, 2005

Project Title: **TRANSFER OF HIGH-CARBON FLY ASH TECHNOLOGY TO CEMENT MANUFACTURING**

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ABSTRACT

CTLGroup, in conjunction with ICCI and DCEO, has worked vigorously to develop and commercialize technology related to the use of high-carbon fly ash in cement manufacturing. A series of commercial-scale demonstrations has confirmed that the technology is viable and applicable to all types of cement manufacturing operations – with proven material, operational, product, energy, and environmental benefits.

During post-demonstration meetings, cement plant personnel unanimously acknowledged the benefits of using high-carbon fly ash in cement manufacturing. However, two underlying issues continually hindered the long-term implementation of the technology. The primary issue was the economical delivery of the fly ash. The secondary issue was the compositional reliability of the fly ash, and its compatibility with the cement plants' raw mix design.

In the current economic climate, it appears that the fly ash producers and cement plants are not willing to compromise on critical positions that would take this technology forward. There seems to be an overriding perception by the fly ash producers that they are not getting the worth of their high-carbon fly ash (i.e. the energy saving factor). The cement plants think they are doing the power plants a favor and so they should be paid to use the fly ash.

A balanced forward-looking approach is required from both sides. The current climate may not yet be conducive to both the cement and power plant economic plans; however, this may be transitory. The fly ash producers need to realize that the landfills are not forever. Eventually with depleting landfill space, the cost of disposal will increase. Similarly, the cement plants also need to realize that the sources for natural raw material will also be depleted and the use of alternative materials will need to be addressed.

To help implement this technology, the federal and state governments could pass legislation that would reward the waste users with "incentives." CTLGroup, ICCI, and DCEO could jointly explore this possibility.

EXECUTIVE SUMMARY

This report describes CTLGroup's ongoing efforts in transferring ICCI-sponsored technology for utilizing high-carbon fly ash from Illinois coal in cement manufacture. The efforts were originally directed toward two Illinois cement plants (Illinois Cement and Cemex-Dixon) and two Illinois power plants (Ameren's Coffeen and Edwards power plants). However, during the course of this project, CTLGroup also worked with other cement and power plants to explore the transfer of this technology.

Teams were formed around a particular cement plant. Within each team, CTLGroup was a technology developer, and ICCI and DCEO were technology promoters. ICCI and DCEO also resolved plant-specific issues on possible infrastructure and process improvements through potential State of Illinois economic development incentives.

The outcome of these efforts was largely as follows:

<u>Team A: Coffeen, Illinois Cement, CTLGroup, ICCI, DCEO:</u> A series of successful demonstrations and repeated team meetings at Illinois Cement led to a plan for infrastructure modification and cost analyses to store and deliver Coffeen fly ash. However, the plan could not move forward for the following reasons; 1) Illinois Cement’s requested grant for developing the infrastructure was too high, 2) Ameren and Illinois Cement could not agree on cost sharing for fly ash transportation, and 3) Illinois Cement cited a compositional change in their limestone quarry, which could not accommodate high usage of fly ash in the raw mix. Nonetheless, CTLGroup remained committed to Illinois Cement for any as-needed offsite/onsite assistance to implement this technology.

<u>Team B: Edwards, Cemex-Dixon, CTLGroup, ICCI, DCEO:</u> Following the successful demonstration using Edwards fly ash at Cemex-Dixon, several meetings took place to resolve logistical issues to implement the technology. Additional samples of fly ash, bottom ash, and slag from Ameren's Edwards, Meridosia, and Coffeen power plants were also collected and characterized for compatibility with the Cemex-Dixon raw mix. The composition of the Meridosia bottom ash appeared suitable for its high alumina and iron contents – but only for a short-term application. Again, the major concern preventing implementation was economical transportation of the fly ash. Alternative nearby sources of suitable fly ash(es) were sought. Bailly and Schahfer plants in Indiana, and the Kapp plant in Iowa were considered, but were again regarded to be uneconomical by Cemex-Dixon.

<u>Team C: Coffeen, Buzzi Unicem (Festus) Cement, CTLGroup, ICCI, DCEO:</u> Since the transport of fly ash was the main issue, the Buzzi Unicem plant in Festus, Missouri, was approached. Festus is a long dry kiln plant. This plant is closer to Coffeen than the Illinois cement plants. After very active initial interest in Coffeen fly ash, Festus personnel cited plant-specific reasons and declined to participate.

<u>Team D: Coffeen, Buzzi Unicem (Cape Girardeau) Cement, CTLGroup:</u> Soon after Festus bowed out, the Cape Girardeau plant in Missouri, expressed interest in using Coffeen fly ash. Since Cape Girardeau is a preheater-precalciner plant, it was critical to conduct a demonstration there because the technology has never been tested in a precalciner plant. Our previous demonstrations have been in long-dry and short-

preheater kilns. The demonstration at Cape Girardeau completed the testing of this technology on all typical cement plant configurations.

Nearly 300 tons of high-carbon fly ash from Coffeen was used at Cape Girardeau. The raw mix composition of the cement plant allowed a 3% addition of the fly ash. The fly ash replaced a significant portion of clay in the raw mix. The demonstration also included stack testing to monitor emissions. The demonstration ran for more than 24 hours and realized several material operational, environmental, and product benefits. Additionally, the cement exhibited better strength properties than the normally produced cements.

<u>Overall Observations:</u> After successful demonstrations at all types of cement plants, our post-demonstration meetings with plant personnel discussed several material, operational, and logistical issues on the implementation of the technology. Although all cement plants realized the overall benefits of using high-carbon fly ash, two underlying issues hindered the implementation. The most critical issue was the economical transportation of fly ash. The second was the compositional reliability of fly ash. Low alkali, low sulfate fly ash was preferred. To help with the implementation, DCEO grants for use of the technology were discussed. The grants were for infrastructure enhancement, but required a commitment to implement the technology. The cement plants were all very interested in the grants, but none would agree to implement the technology.

From the meetings, it seemed that the power plants would rather discard fly ash in landfills instead of sharing the delivery cost with cement plants. The cement plants also did not want to share the transportation cost. The general attitude was that since they are “helping” the power plants dispose of their fly ash, they are entitled to an “incentive” instead of sharing in the transportation cost. Based on this, the current climate does not appear to be conducive to the cement and power plant economics. Sooner or later, landfill space and natural resources will diminish. At this time, the technology will be sought by both power and cement plants.

We believe that the federal and state governments could also be approached for the passage of legislation to reward the waste users with economical incentives. CTLGroup, ICCI, and DCEO could form a consortium to explore this possibility at the state level.

As a team, CTLGroup, ICCI, and DCEO, have worked vigorously to develop and demonstrate this technology. It is only a matter of time that both cement and power plant will realize its usefulness and consider adopting it.

OBJECTIVES

With the ICCI sponsored 1988-2002 projects on the use of high-carbon fly ash in cement manufacture, CTLGroup has been able to generate a widespread interest for high-carbon fly ash technology among cement plants. The objective of this project was to resolve these issues so that the technology can be successfully and fully implemented. To identify, address, and resolve these issues, CTLGroup worked with the previously formed technology-transfer teams. The teams were:

Team 1 - Ameren's Coffeen Power Station, Illinois Cement, CTLGroup, ICCI, DCEO

Team 2 - Ameren's Edwards Power Station, Cemex-Dixon, CTLGroup, ICCI, DCEO

In order to achieve the objective, other potential teams were also included. These were:

- Ameren's Coffeen Power Station, Buzzi Unicem USA (Festus), CTLGroup, ICCI, DCEO
- Ameren's Coffeen Power Station, Buzzi Unicem USA (Cape Girardeau), CTLGroup, ICCI, DCEO

The team members, in their capacities, attempted to identify and resolve the issues related primarily to material, operation, products, and environment.

CTLGroup provided both offsite/onsite technical support and expert assistance to the participating plants. The most common issues were related to:

- Materials – fly ash composition vs. raw materials, mix design formulations
- Production – fly ash composition vs. production and cement quality
- Emissions – fly ash vs. emissions (NO_x, SO_x, O_2, CO, CO_2, THC)
- Environments – tracking trace metals including mercury in fly ash, raw feed, clinker, and cement kiln dust

The role of CTLGroup was the technology developer, whereas those of the ICCI and DCEO were the technology promoters. ICCI and DCEO were also to assist in addressing plant-specific and material issues with potential incentives for the necessary system modifications through grants. CTLGroup's involvement as the technology developer was also to organize team meetings on as-needed basis to ensure that the teams were able to resolve the impending issues for implementation of the technology.

INTRODUCTION AND BACKGROUND

Of the nearly 3 million tons of fly ash annually produced in Illinois, less than two-thirds is used in commercial products – the remainder is landfilled. Although some fly ash can be utilized in concrete, much of the landfilled ash is not usable in concrete. The main reason is high-carbon contents. The continued implementation of the environmental policies to reduce NO_x emissions at coal-fired power plants will further increase the production of fly ash with significantly higher carbon contents.

Since fly ash is rich in silica, alumina, and iron contents, it can be conveniently used in raw feed for cement manufacturing, while the unburned carbon in the fly ash could contribute as fuel supplement. Our ICCI sponsored projects have demonstrated the concept both at laboratory and commercial-scale. The commercial-scale demonstrations have involved Illinois cement plants using Illinois coal fly ash from local power plants.

This report details CTLGroup's ongoing efforts on use of high-carbon fly ash in cement manufacturing and discusses implementation aspects of the technology at the participating cement plants. The report also discusses the logistical issues involved in transferring the technology to full-scale commercialization.

EXPERIMENTAL PROCEDURE

The characterization of fly ash and raw materials from the participating power and cement plants, and the evaluation of clinker and cement produced during the demonstration were carried out at the CTLGroup facilities. Fly ash, raw material, raw mix design, clinker, and cement were analyzed using X-ray fluorescence (XRF), X-ray diffraction (XRD), and differential scanning calorimetry (DSC). The evaluation of clinker was also supplemented by the microscopic examination of its polished sections. Trace metals were determined by wet chemical analyses using inductively coupled plasma (ICP) technique. Mercury was determined using direct mercury analyzer (DMA) methodology.

RESULTS AND DISCUSSION

PHASE I

The project started with the organization of technology team meetings to address specific issues relating to the technology transfer. The goals of meetings were to resolve any utility- and/or cement plant-specific issues that hinder or restrict the full implementation of this technology.

Task 1. Individual Team Meetings, Identifying, and Addressing Issues

As mentioned earlier the two technology teams involving the cement plants and power stations were:

1) Ameren's Coffeen Power Station, Illinois Cement, CTLGroup, ICCI, DCEO
2) Ameren's Edwards Power Station, Cemex-Dixon, CTLGroup, ICCI, DCEO

The role of CTLGroup was the technology developer, and that of the ICCI and DCEO was the technology promoter. The roles of ICCI and DCEO was paramount in terms of potential economic incentives and matching funding from the State of Illinois programs for plant infrastructure modifications on as-needed basis.

Coffeen (Ameren), Illinois Cement: Follow up discussions on the earlier meetings between Illinois Cement and Coffeen were held to resolve the impending issues on the fly ash transportation cost analyses, as well as the infrastructure modifications to store and convey fly ash into the plant operating system. However, the discussions with Illinois Cement were put on hold as a consequence of 1) the negotiations between Illinois Cement and Ameren on the transportation cost could not move forward, 2) the infrastructure cost for modifying the fly ash storage and delivery system presented by Illinois Cement to DCEO was too high, and 3) Illinois Cement reported a compositional change in their limestone quarry that will limit the use of Coffeen fly ash in the raw mix.

Coffeen (Ameren), Cemex-Dixon Cement: After several contacts and meetings with individuals from Cemex-Dixon Cement and Ameren, CTLGroup organized a face-to-face meeting of Cemex-Dixon plant personnel, Cemex (corporate) personnel, and Ameren (corporate) personnel. The meeting was held on January 2004 at the Cemex-Dixon plant. Both short- and long-term logistical issues for implementing the high-carbon fly ash technology were addressed. During the meeting, the use of bottom ash/slag was also discussed to address an immediate need for the plant that would also tie into their long-term plans for the implementation of the high-carbon fly ash technology.

As a result of the meeting, Cemex corporate personnel visited Ameren's Edwards, Meridosia, and Coffeen power plants. Cemex personnel obtained samples of fly ash, slag, and bottom ash, and shipped them to CTLGroup for analyses. The results of the analyses are presented in Table 1.

Table 1. Composition of fly ash, slag, and bottom ash from Ameren's Coffeen, Edwards, and Meredosia Power Plants

Materials	Coffeen		Edwards		Meredosia	
	Fly Ash	Slag	Bottom Ash	Fly Ash	Bottom Ash	Bottom Ash
SiO_2	46.65	54.87	51.94	53.63	42.08	42.35
Al_2O_3	17.11	20.62	19.51	22.16	15.08	13.57
Fe_2O_3	6.39	8.21	15.73	8.87	23.33	27.83
CaO	3.27	10.17	5.05	3.63	7.51	5.67
MgO	1.25	1.58	1.20	1.05	1.61	0.81
SO_3	0.17	0.08	0.25	0.83	1.40	1.46
Na_2O	1.66	1.01	1.01	1.32	0.61	0.59
K_2O	2.60	1.95	1.74	1.79	1.38	1.51
TiO_2	1.11	0.83	0.88	1.00	0.89	0.72
P_2O_5	0.24	0.09	0.25	0.38	0.28	0.14
Mn_2O_3	0.05	0.06	0.06	0.04	0.07	0.12
SrO	0.05	0.06	0.08	0.10	0.07	0.01
Cr_2O_3	0.03	0.02	0.02	0.02	0.03	0.03
ZnO	0.09	0.01	0.03	0.03	0.07	0.06
LOI (950°C)	18.37	0.13	1.64	4.70	4.95	4.94
Total	99.04	99.67	99.39	99.56	99.34	99.82
Alkalies*	3.37	2.29	2.15	2.50	1.52	1.59

*Alkalies as Na_2O equivalent

Cemex-Dixon showed interest in the use of bottom ash from Meredosia because of its high iron contents, but decided against it due to unfavorable distance and the cost involved in transportation.

Since the economics of transportation was the issue, alternative Illinois coal fly ash sources were identified. The power plants and their relative distances from Cemex-Dixon, coal usage, and their capacities are shown in Table 2.

Table 2. Alternative Power Plants Considered for Cemex-Dixon

Power Plants	Location	Distance to Cemex-Dixon	Yearly Fly Ash Production	Coal usage
Schahfer Station	Wheatfield, IN	200 miles	150K tons	70% IL coal
Bailly Station	Chesterton, IN	150 miles	50-60K tons	90% IL coal
Kapp Station	Clinton, IA	50 miles	20K tons	Mostly IL coal

The carbon content in Schahfer and Bailly fly ashes ranged between 6-10%. After reviewing the information, Cemex-Dixon cement decided against the use of these materials citing, yet again, uneconomical transportation. Fly ash from the closely located Kapp Station, though higher in carbon, was not attractive because the available quantity was too small for Cemex-Dixon.

Ameren's Coffeen Power Station, Buzzi Unicem USA (Festus), CTLGroup: Since the transportation of fly ash to Cemex-Dixon cement appeared to be the main economic issue, CTLGroup considered cement plants in the neighboring state of Missouri for the exploration of high-carbon fly ash from Coffeen.

Buzzi Unicem USA cement plants in Festus and Cape Girardeau, were contacted. Both plants showed active interest in using the Coffeen fly ash. However, Festus, being closer, was preferred. The distance between the plants is about 100 miles. Upon request, Coffeen fly ash samples collected during August and September 2004 were sent to the Festus plant for in-house analyses.

The composition of the cement plant raw materials could allow up to 3% addition of the Coffeen fly ash. After several discussions, visits, and meetings with the Festus plant personnel, a 56-hour demonstration test involving nearly 400 tons of fly ash from Coffeen was agreed upon in March 2005. However, citing plant-specific reasons, Festus personnel cancelled the demonstration. Consequently, CTLGroup contacted the Cape Girardeau cement plant to explore implementing the technology using Coffeen fly ash.

Ameren's Coffeen Power, Buzzi Unicem USA (Cape Girardeau), CTLGroup: As a result of a series of vigorous discussions, meetings, and personnel visits, CTLGroup worked with the Cape Girardeau plant to organize and conduct a longer-term demonstration using fly ash from Coffeen. The demonstration took place in June 2005. Nearly 300 tons of high-carbon ash was used in a 24-hour long demonstration. The demonstration at Cape Girardeau plant also included stack (emissions) tests. For comparison, emission data were collected before the demonstration. Details of the demonstration and outcome of the follow up discussions on the technology implementation are given in the forthcoming sections.

PHASE II

Task 2. Material Characterization and Mix Designs for Demonstrations

Although the eventual demonstration took place using Coffeen fly ash at the Cape Girardeau cement plant, a demonstration was planned at the Festus cement plant by virtue of their active interest in exploring the technology.

Planned Festus-Coffeen Demonstration

Festus is a long kiln cement plant. In order to formulate a suitable raw mix using Coffeen fly ash, a typical raw mix from Festus plant was acquired and analyzed for oxide composition. Table 3 presents the raw mix from the Festus cement plant.

Table 3. Typical Raw Mix of the Festus Cement Plant

Analyte, wt%	Raw mix	
	As received	Ignited Basis
SiO_2	13.70	20.95
Al_2O_3	3.15	4.81
Fe_2O_3	2.30	3.52
CaO	42.29	64.68
MgO	1.93	2.95
SO_3	0.32	0.49
Na_2O	0.16	0.24
K_2O	0.31	0.47
TiO_2	0.19	0.28
P_2O_5	0.09	0.14
Mn_2O_3	0.10	0.15
SrO	0.04	0.06
Cr_2O_3	0.10	0.15
ZnO	0.12	0.18
L.O.I. (950ºC)	34.29	0.00
Total	99.07	99.07
Alkali as Na_2O	0.36	0.55

Four samples of Coffeen fly ash, collected by CTLGroup between August and September 2004, were considered for use in the Festus demonstration. Their oxide analyses are presented in Table 4.

Table 4. Composition of Coffeen Fly Ashes for the Planned Festus Demonstration

Analyte, wt%	Sample 1	Sample 2	Sample 3	Sample 4	Avg.
SiO_2	51.25	50.00	49.93	49.63	50.20
Al_2O_3	19.02	18.61	17.98	18.34	18.49
Fe_2O_3	7.38	7.75	7.4	7.64	7.54
CaO	4.30	3.74	3.91	4.74	4.17
MgO	1.36	1.24	1.27	1.49	1.34
SO_3	0.42	0.45	0.35	0.56	0.45
Na_2O	2.11	2.26	2.09	2.16	2.16
K_2O	2.78	2.81	2.73	2.71	2.76
TiO_2	1.17	1.20	1.15	1.17	1.17
P_2O_5	0.20	0.20	0.19	0.22	0.20
Mn_2O_3	0.05	0.04	0.04	0.04	0.04
SrO	0.05	0.05	0.05	0.07	0.06
Sr_2O_3	0.03	0.03	0.03	0.03	0.03
ZnO	0.15	0.16	0.14	0.14	0.15
L.O.I. (950ºC)	10.55	11.09	12.16	10.72	11.13
Total	100.82	99.63	99.43	99.66	99.88
Alaklies as Na_2O	3.94	4.11	3.89	3.94	3.97

The nature of Festus plant raw materials permitted 3% fly ash addition to their raw mix. A 3% addition of fly ash to the raw mix gave the following formulation (see Table 5). The raw mix without fly ash (from Table 3) is also given in Table 5 for comparison.

Table 5. Raw Mix Composition with and without 3% Coffeen Fly Ash

Analyte, wt%	Raw Mix with 3% Fly Ash	Raw Mix without Fly Ash
SiO_2	22.07	20.95
Al_2O_3	5.24	4.81
Fe_2O_3	3.65	3.52
CaO	63.07	64.68
MgO	2.91	2.95
SO_3	0.49	0.49
Na_2O	0.29	0.24
K_2O	0.54	0.47
TiO_2	0.31	0.28
P_2O_5	0.14	0.14
Mn_2O_3	0.15	0.15
SrO	0.06	0.06
Cr_2O_3	0.15	0.15
ZnO	0.18	0.18
L.O.I. (950ºC)	0.00	0.00
Total	99.43	99.07
Alkali as Na_2O	0.64	0.55

The calculated phase distributions of the resulting clinkers are given in Table 6.

Table 6. Phase Composition of Clinkers from Festus Raw Mix with and without Fly Ash

Analyte, wt%	Raw Mix with 3% Fly Ash	Raw Mix without Fly Ash
C_3S	49	65
C_2S	27	11
C_3A	8	7
C_4AF	11	11

Shortly before the demonstration, Festus plant personnel cited plant-specific reasons and cancelled the demonstration.

Cape Girardeau-Coffeen Demonstration

The demonstration at the Cape Girardeau plant in Missouri (Figure 1) consumed nearly 300 tons of Coffeen fly ash in 24 hours at a rate of up to 3% addition. The plant's raw material composition could only allow this level of addition. The fly ash addition primarily substituted for clay in the raw feed.

Figure 1. Cape Girardeau Cement is a Preheater-Precalciner Kiln Plant
(Inset showing the rotary kiln)

The raw materials used in the Cape Girardeau cement plant and their compositions are given in Table 7; the composition of Coffeen fly ash is also included for comparison.

Table 7. Composition of the Cape Girardeau Plant Raw Materials and Coffeen Fly Ash

Materials	Tripoli “Sand”	Diaspore Clay	Limestone	Coffeen Fly Ash
SiO_2	94.24	41.22	3.18	50.74
Al_2O_3	2.50	35.48	0.81	19.52
Fe_2O_3	1.46	5.89	0.29	6.99
CaO	< 0.01	0.19	52.31	5.56
MgO	0.10	0.43	1.41	1.65
SO_3	< 0.01	0.09	0.32	0.93
Na_2O	< 0.01	< 0.01	0.06	2.08
K_2O	0.16	0.96	0.25	2.83
TiO_2	0.11	1.76	0.04	1.25
P_2O_5	0.07	0.15	0.02	0.27
Mn_2O_3	0.04	0.03	0.01	0.09
SrO	< 0.01	0.10	0.02	0.10
Cr_2O_3	0.03	0.06	< 0.01	0.05
ZnO	0.03	0.02	< 0.01	0.19
LOI (950°C)	1.35	13.36	42.00	7.28
Total	100.09	99.74	100.71	99.53
Alkalies as Na_2O	0.11	0.63	0.23	3.94

The fly ash was also tested by differential scanning calorimetry (DSC) to determine fuel value and presence of any organic volatile species related to emissions. The DSC plot in Figure 2 shows the fuel value of 346 J/g. Absence of any peak(s) below 350^{o}C also confirmed that there is no emission-related species in the ash. Also of interest is the negative hump below 470^{o}C. This property is useful as a heat sink as it reduces temperature in the upper preheater stages leading to clearer passage for raw feed flow.

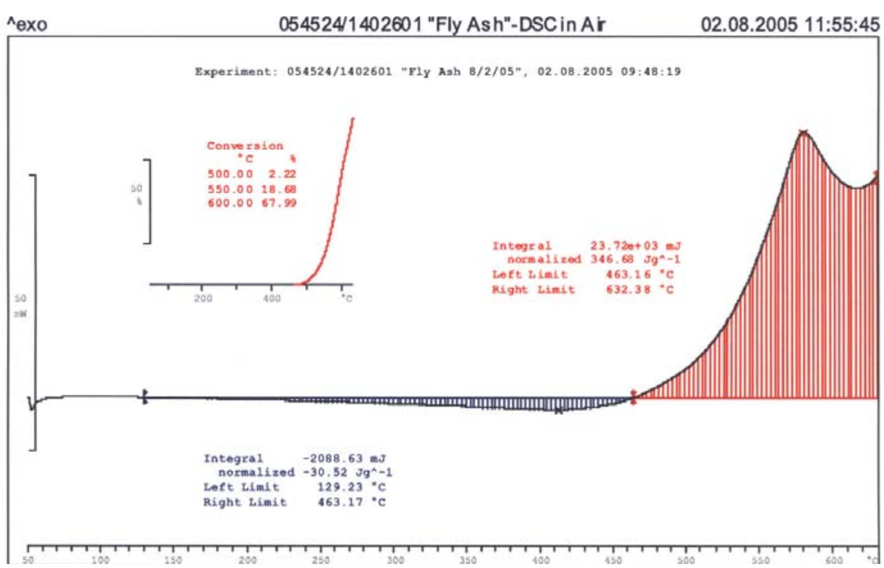


Figure 2. DSC Plot of the Coffeen Fly Ash Used in the Demonstration

The raw mix composition tested during the demonstration at Cape Girardeau used 3% Coffeen fly ash as shown in Table 8. Regular raw mix (without fly ash) is also shown for comparison.

Table 8. Cape Girardeau Raw Mix with and without 3% Coffeen Fly Ash

Materials	Regular Raw Mix (without Fly Ash)	Raw Mix with 3% Coffeen Fly Ash
SiO_2	21.18	20.94
Al_2O_3	5.12	5.64
Fe_2O_3	3.12	2.99
CaO	65.23	65.39
MgO	2.94	3.00
SO_3	1.00	1.12
Na_2O	0.12	0.13
K_2O	1.04	1.15
TiO_2	0.23	0.22
P_2O_5	0.07	0.07
Mn_2O_3	0.05	0.05
SrO	0.05	0.06
Cr_2O_3	<0.01	<0.01
ZnO	<0.01	0.02
LOI (950°C)	0.00	0.00
Total	100.15	100.77
Alkalies as Na_2O	0.81	0.88

It should be noted that the raw mix compositions with or without the use of 3% fly ash do not differ significantly. The fly ash mostly replaced clay in the regular raw mix, which is similarly rich in SiO_2, Al_2O_3, and Fe_2O_3. The alkali levels of both the raw mixes are also similar.

Task 3. Evaluation of System Modifications via Demonstration and Trouble Shooting

During the demonstration at Cape Girardeau, fly ash was introduced into the air stream after the raw mill to the blending silos. With the current level of fly ash addition, this arrangement seems satisfactory and requires little system modifications. However, the plant would welcome any infrastructure modifications in the system that enhanced the utilization of high-carbon Coffeen fly ash and improved operational efficiency. The plant presented the following options:

Pumping Fly Ash into the Precalciner: For a higher level of high-carbon fly ash addition, the plant would prefer pumping the material directly into the precalciner to have a more pronounced impact on fuel savings. This would require a separate storage silo for the ash and a separate pumping system. This would also involve re-plumbing of the existing storing, delivery, and pumping systems.

Insuflation of Fly Ash into the Kiln: For even higher-carbon fly ashes, the plant envisages insuflating the ash directly into the rotary kiln. This would require installing a separate storage facility and a separate air stream for the pumping system.

Infrastructure Modification at Southern Illinois Power Cooperative Plant in Marion: Cape Girardeau personnel specifically pointed out that an even better and logistically viable move would be to modify the infrastructure at the Southern Illinois Power Cooperative plant in Marion. Marion is less than 50 miles from Cape Girardeau – much closer than the Coffeen plant. The modifications needed at Marion would be to 1) develop a system to separately collect fly ash from the rest of the combustion by-products, and 2) install an oxidizing system to convert sulfite-rich into sulfate-rich sludge that can also be used in cement finish milling. Cape Girardeau can benefit from both of these materials.

Task 4. Trace Metal and Mercury Analyses

The Coffeen fly ash used in the demonstration was tested for trace metals. Also tested were the raw mix, clinker, and cement kiln dust. The analyses included several of the RCRA (Resource Conservation and Recovery Act) metals such as arsenic, selenium, lead, mercury, cadmium, nickel, and chromium. Because of recent concerns over mercury in fly ash and its effect on the environment, particular emphasis was given to the determination of mercury. The samples were collected before, during, and after the demonstration to make a reasonable comparison on the trace metal levels to determine the effects of fly ash incorporation. The data are shown in Tables 9 and 10.

Table 9. Trace Metals in Fly Ash and Cement Raw Mixes from the Cape Girardeau Plant Collected During the Demonstration (ppm)

Trace Metals	Fly Ash	Raw Mix Before	Raw Mix During	Raw Mix After
Mercury	0.066	3.08	2.81	3.76
Antimony	16.82	< 1.60	< 1.59	< 1.61
Arsenic	156.10	< 2.08	4.83	< 2.08
Barium	466	70.6	90.6	68.3
Beryllium	11.450	< 0.06	< 0.06	< 0.06
Cadmium	8.17	< 0.06	< 0.06	< 0.06
Chromium	122.6	16.8	13.700	19.1
Lead	100	< 0.59	< 0.59	< 0.59
Nickel	170.9	12.3	11.9	15.0
Selenium	7.1	< 2.55	< 2.53	< 2.56
Silver	< 0.12	< 0.12	< 0.12	< 0.12
Thallium	< 1.30	< 1.31	< 1.30	8.34
Zinc	493	25.7	76.6	169
Vanadium	156.2	23.6	23.3	28.6
Copper	115	46.6	29.7	44.8
Cobalt	29.12	< 0.12	< 0.12	2.15

Table 10. Trace Metal in Clinkers and CKD Collected from the Cape Girardeau Plant During the Demonstration (ppm)

Trace Metals	Clinker Before	Clinker During	Clinker After	CKD Before	CKD During	CKD After
Mercury	0.018	0.009	0.008	0.228	0.191	0.051
Antimony	4.42	3.10	12.0	5.00	6.46	9.50
Arsenic	11.8	7.32	20.8	6.21	6.06	7.64
Barium	175	175	171	145	122	97.6
Beryllium	0.695	0.557	< 0.06	< 0.06	< 0.06	< 0.06
Cadmium	< 0.06	< 0.06	< 0.06	9.56	8.76	4.16
Chromium	50.1	49.0	47.3	30.7	34.7	24.8
Lead	21.6	15.8	3.32	547.9	506	379
Nickel	34.2	32.3	38.4	17.17	18.8	24.4
Selenium	< 2.55	< 2.57	< 2.56	40.24	34.3	4.56
Silver	< 0.12	< 0.12	< 0.12	81.8	72.5	47
Thallium	< 1.31	< 1.31	< 1.31	< 1.30	< 1.31	47.3
Zinc	139	138	211	218	250	281
Vanadium	46.3	46.1	72.6	26.1	29.9	49.7
Copper	95.5	94.8	98.4	121	122	131
Cobalt	7.28	7.20	5.28	3.83	3.82	1.56

It should be noted that fly ash may have higher levels of trace metals but its total mercury content is significantly lower than the raw mixes (prepared with and without fly ash addition). Mercury and most other trace metals in clinkers and CKDs produced during the demonstration do not differ significantly from those produced before and after the demonstration.

Task 5. Stack Emission Testing

Stack emission tests were also carried out during the demonstration to assess the effect(s) of the use of high-carbon fly ash on cement operation. Stack emissions were monitored for of NO_x, SO_x, CO, CO_2, O_2, and total hydrocarbons (THC). The test was aimed at critically examining the effect of unburned high-carbon (and any associated organic/volatile matter) in the fly ash on cement plant stack emissions. The tests were conducted before and during the demonstration.

Data on the baseline and mean values of stack emissions concentrations during the demonstration with fly ash are summarized in Table 11 and in Figure 3 as follows.

Table 11. Stack Emission Data During Demonstration at Cape Girardeau Plant

Pollutants (concentration)	O_2 (%)	CO_2 (%)	NO_x (ppm)	SO_2 (ppm)	CO (ppm)	THC (ppm)
Baseline*	9.59	17.43	306.42	55.41	1232.11	151.20
Demonstration	9.95	18.45	271.92	35.44	1670.76	155.29

* Based on data before the demonstration

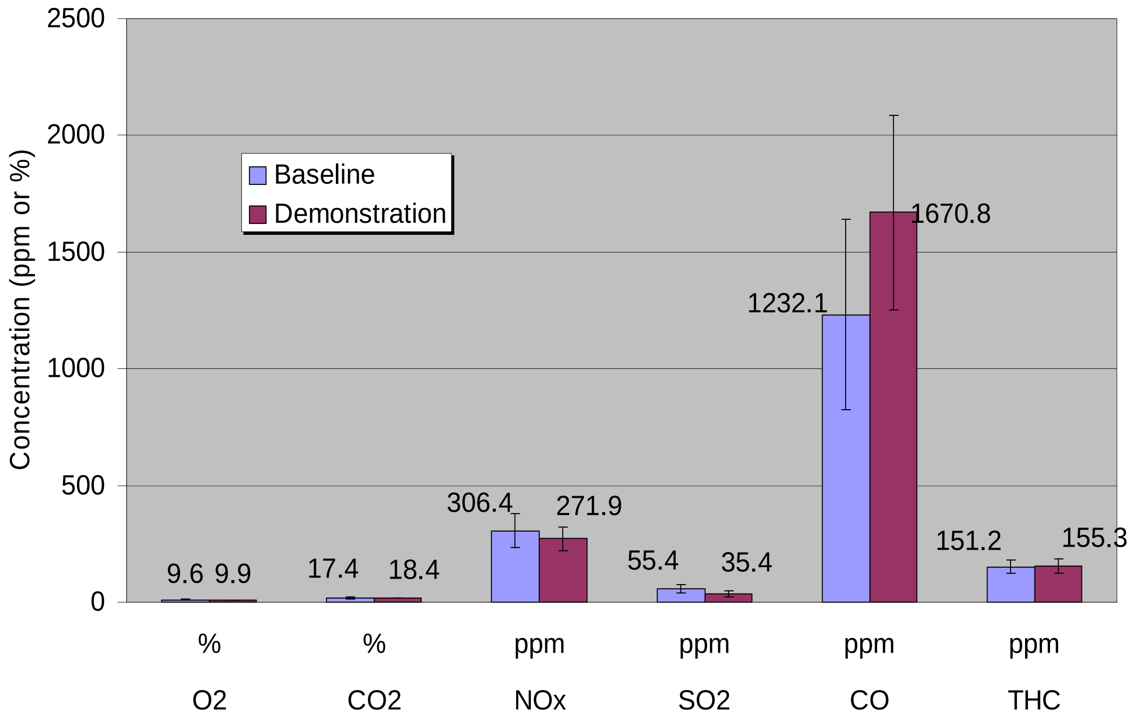


Figure 3. Stack Emission Data During Demonstration at Cape Girardeau Plant

It should be noted that the concentration levels during most of the demonstration were lower than the baseline. In fact, the levels of both SO_2 and NO_x were significantly lower than the baseline for the time period during which the fly ash was included in the raw mix; the only exception appears to be CO concentration. THC emissions were not changed significantly. Similarly O_2 and CO_2, which were very low throughout, did not vary significantly.

Task 6. Testing and Evaluation of Clinker and Cement

Clinkers and cements produced during the demonstration were tested and evaluated. Clinkers were examined for mineralogical composition and major phase distribution. Cements produced from these clinkers were tested for compliance with ASTM C 150 specifications.

Clinker Characterization**:** The clinkers produced before, during, and after demonstration were analyzed by X-ray fluorescence (XRF) method for oxide analysis and to compute Bogue composition. The clinkers were subsequently tested for their mineralogical composition by the X-ray diffraction (XRD) method, and examined for major phase distribution by reflected microscopy. Their oxide analyses and computed Bogue compositions are shown in Table 12.

Table 12. Clinker Composition Before, During, and After the Demonstration

Analyte, wt%	Before	During	After
SiO_2	22.18	21.87	22.19
Al_2O_3	4.62	4.71	4.74
Fe_2O_3	3.05	3.27	3.17
CaO	65.20	64.68	64.52
MgO	2.94	3.02	3.28
SO_3	0.98	1.10	0.76
Na_2O	0.13	0.15	0.13
K_2O	0.80	0.93	0.70
TiO_2	0.24	0.27	0.28
P_2O_5	0.06	0.05	0.05
Mn_2O_3	0.09	0.08	0.09
SrO	0.07	0.07	0.06
Cr_2O_3	<0.01	<0.01	<0.01
ZnO	0.02	0.03	0.04
L.O.I. (950^{o}C)	0.07	0.14	0.12
Total	100.43	100.36	100.13
Calculated Bogue Compounds			
C_3S	59	58	56
C_2S	19	19	22
C_3A	7	7	7
C_4AF	9	10	10

The data from Bogue composition and the subsequent XRD analysis (Figure 4) confirmed the presence of major C_3S, C_2S, C_3A, and C_4AF phases in the clinkers.

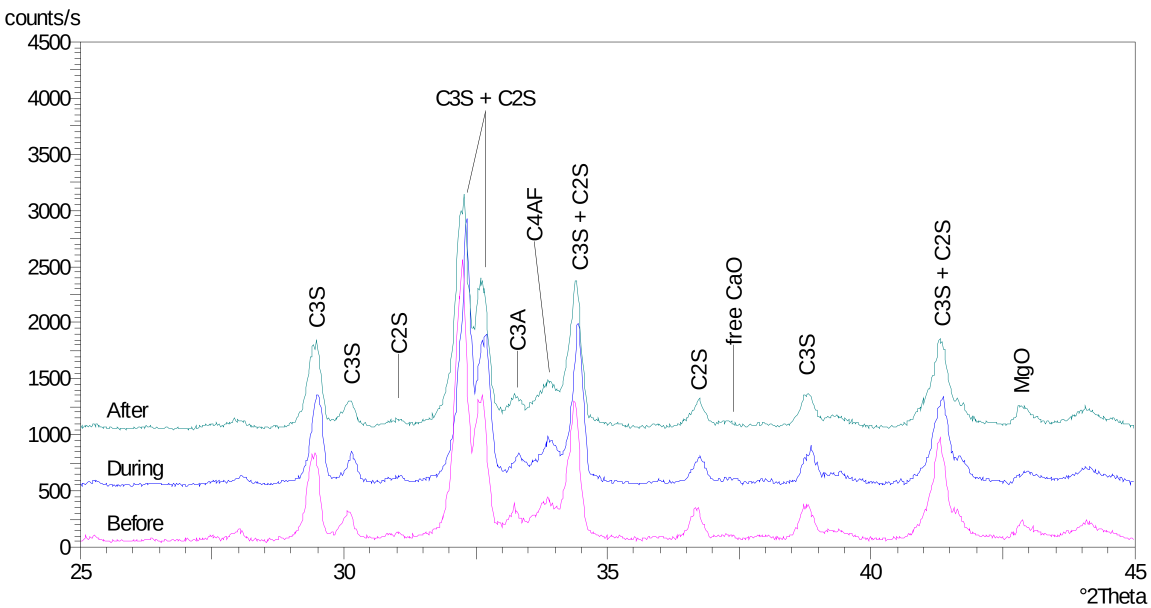
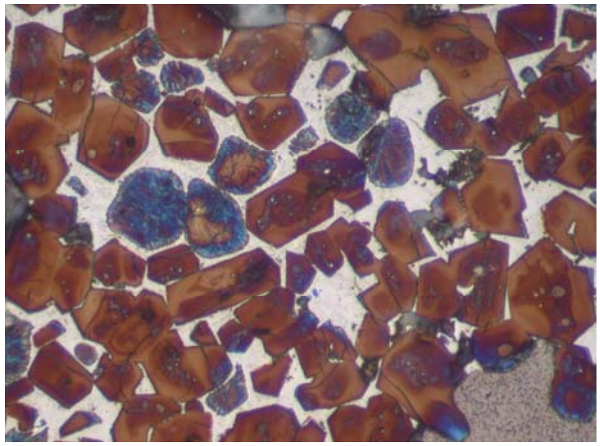
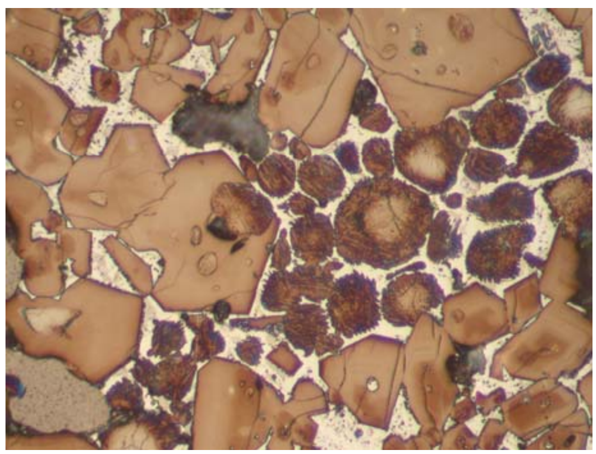


Figure 4. XRD Patterns of Clinkers Produced Before, During, and after Demonstration

The XRD data appear identical for all clinkers, suggesting similarity of the raw mix formulations before, during, and after the demonstration. The photomicrographs of the clinkers produced before, during, and after the demonstration also show typical distribution of the major clinker phases (Figure 5).

a)


b)


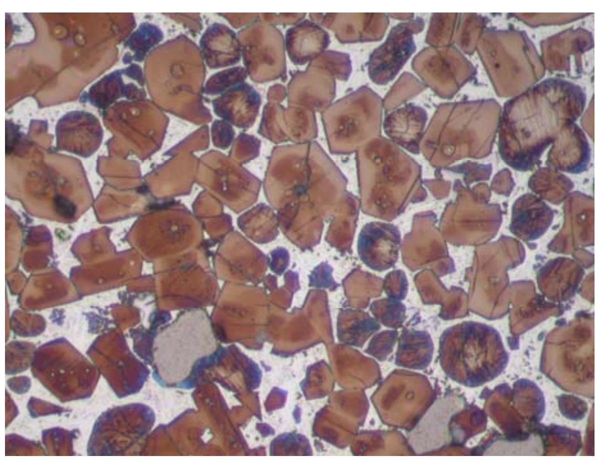
c)


Figure 5. Photomicrographs of Clinker a) Before Demonstration, b) During Demonstration (with Fly Ash), and c) After Demonstration. Field Length = 280 microns.

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

As can be seen in clinkers produced during the demonstration (Figure 5b), alite crystals are larger and cannibalistic (crystals are “glued” together along exterior edges), than in clinkers before and after the burn. This can be attributed to higher clinkering temperature caused by the addition of high-carbon fly ash in the raw mix. Belite crystals are moderate in size, with ragged edges indicative of slow cooling.

<u>Cement Production, Testing, and Evaluation:</u> The clinkers produced before, during, and after the demonstration were ground with appropriate amounts of gypsum to produce cements. Cement compositions are given in Table 13.

Table 13. Cement Composition Produced During the Demonstration

Analyte, wt.%	Cement Before	Cement During	Cement After
SiO_2	21.10	20.76	21.06
Al_2O_3	4.48	4.45	4.58
Fe_2O_3	3.20	3.36	3.23
CaO	63.44	63.11	62.52
MgO	2.81	2.87	3.14
SO_3	2.91	3.02	2.96
Na_2O	0.11	0.08	0.09
K_2O	0.66	0.72	0.68
TiO_2	0.23	0.26	0.26
P_2O_5	0.06	0.06	0.05
Mn_2O_3	0.09	0.09	0.08
SrO	0.07	0.07	0.07
Cr_2O_3	<0.01	<0.01	<0.01
ZnO	0.01	0.03	0.04
L.O.I. at 950°C	1.07	1.02	1.09
Total	100.24	99.87	99.87
Alkalies as Na_2O	0.54	0.55	0.53
Calculated Bogue Compounds			
C_3S	55	56	51
C_2S	19	17	22
C_3A	6	6	7
C_4AF	10	10	10

The composition confirms these cements meet the requirements of ASTM C150 for Type I/II cements. The analyses also confirmed that an addition of 3% fly ash to the raw mix did not vary the levels of alkalies and sulfate in the demonstration cement.

These cements were tested and evaluated in accordance with the ASTM C 150 specifications. The results are shown in Table 14.

Table 14. ASTM C 150 Data on Demonstration Cements

	Before	During	After	*ASTM limits
ASTM C 204 - Fineness, air permeability (Blaine), m^2/kg				
	357	363	366	280 (min)
ASTM C 109 - Compressive strength, psi				
3-day	3730	4150	3650	+1740 (min)
7-day	4630	4760	4320	+2760 (min)
28-day	5860	6020	5770	+4060 (min)
ASTM C 191 – Vicat time of set, minutes				
Initial	170	130	125	45 (min)
Final	250	210	210	375 (max)
ASTM C 185 – Air content, %				
	5	7	7	12 (max)
ASTM C 151 – Autoclave expansion, %				
	0.012	0.02	0.06	0.80 (max)

* ASTM limits for Type I/II cements; + ASTM limits for Type I cements

It is evident from the data that the cement produced during demonstration complied with the requirements established by ASTM C 150 specification. However, the demonstration cement has better strength performance than the other cements at all ages. The time of set, air contents, and autoclave results were normal for the demonstration cement.

PHASE III

Task 7. Evaluation of Technology Transfer from Demonstration Data

The results from the Cape Girardeau demonstration were discussed with the plant technical personnel with a goal of implementation. Some selected critical observations and the realized benefits shared with the plant included:

- 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) and SO_2 reduced
- Energy saving of 3% at the raw mill realized
- Clinker and cement qualities improved

To the question of using the high-carbon fly ash on long-term basis, the Cape Girardeau responded that they would be willing to consider the technology given that the following issues are addressed:

- Economical fly ash transportation: The fly ash from Coffeen needs to be delivered to the plant at competitive cost as compared to the other similar materials currently being delivered to the plant.
- Preference for low-alkali fly ash: Since the plant produces low alkali cement, they would prefer a low-alkali fly ash. Their current limestone quarry, already high in alkalies, only warrants a low substitution of alkali-containing alternative materials. However, in the future (within 9-12 months), limestone from their new

quarry will be significantly low in alkalies that may allow a higher use of up to 7% fly ash.

- Compositional reliability for incorporation in the raw mix: The composition of the fly ash needs to be consistent and compatible with the cement plant raw mix.

Cape Girardeau also acknowledged that any effort on the improvement/modifications in the system would certainly be favorably looked at. It was pointed out that for a higher level of high-carbon fly ash addition, the plant would prefer pumping the material directly into the precalciner to realize a more pronounced fuel saving. This may require a separate silo and a separate pumping system, which would involve re-plumbing of the existing storing, delivery, and pumping system. For even higher carbon fly ashes, the plant envisages insuflating directly into the kiln, which again would require a separate storage and pumping system.

In the same context, the Cape Girardeau plant specifically mentioned that infrastructure modifications at the Southern Illinois Power Cooperative in Marion would be both economically and logistically viable. Marion is less than 50 miles from Cape Girardeau. The specific modifications needed at Marion would be, 1) developing a structure to separately collect and transport the fly ash from the rest of the combustion by-products, and 2) install an oxidizing system to convert the sulfite-rich into sulfate-rich sludge, which can be also used in cement finish milling. Cape Girardeau may benefit from both of these by-products.

CONCLUSIONS AND RECOMMENDATIONS

As a result of several successful commercial-scale demonstrations, both previous and present, on the use of fly ash technology, the logistics for implementing the technology were vigorously addressed in joint technical meetings between the key personnel from the cement plants, the partnering fly ash producers, CTLGroup, ICCI, and DCEO. The meetings were organized to particularly resolve material, operational, and plant-specific issues.

With the demonstration at Cape Girardeau, a preheater-precalciner cement plant, we have shown that this technology can be utilized at all typical types of cement plants. The demonstration at Cape Girardeau also confirmed the benefits of the high-carbon fly ash technology in terms of material, energy, and environmental benefits.

Cape Girardeau, like the other participating plants, expressed particular concerns when it came to the economics of material transportation. To a lesser extent, the compositional reliability of the fly ash was also a concern. Other issues mentioned by the cement plants are, 1) consistency of fly ash composition, and 2) the reliability of the supply.

Based on our meetings with both fly ash producers and cement plants, an overriding perception by the fly ash producers is they are not getting the worth of their high-carbon fly ash (i.e. the energy value factor). They can continue to landfill the fly ash cheaper than transporting it to cement plants. The cement plants feel they are doing a favor by using “waste” fly ash so they should be entitled to an incentive.

Together, these views have prevented the technology from being implemented. To get the technology implemented, there needs to be a balanced forward-looking approach from both sides. The current climate may not yet be conducive to both the cement and power plant economic plans; however, this is transitory. The fly ash producers need to realize that with depleting landfill space, the cost of disposing material will increase. Similarly, the cement plants also need to realize that the sources for natural raw materials will also be depleted and the use of alternative materials will need to be eventually addressed. It is only a matter of time before both cement and power plants will realize the usefulness of this technology and implement it.

To help speed the process, CTLGroup believes that the federal and state governments could pass legislation that would reward the waste users with economic incentives. CTLGroup, ICCI, and DCEO could form a consortium to explore this possibility at the state level.

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