FINAL TECHNICAL REPORT
September 1, 2002, through July 31, 2004

Project Title: **UTILIZATION OF ILLINOIS FLY ASH IN MANUFACTURING OF CERAMIC TILES**

ICCI Project Number: 02-1/3.1A-8
Principal Investigator: Alex Mishulovich, CTL Inc.
Project Manager: Francois Botha, ICCI

ABSTRACT

Experimental work in this project concentrated on refinement and finalization of the mix composition and process parameters. It focused on preparations for the demonstration run on the commercial type equipment at the TCA facility at Clemson University.

Some further refinements of the technology were investigated. In order to increase the tile body density without a temperature increase, modified mix compositions were tested. As a standard procedure, tiles were measured for drying and firing shrinkage and subjected to physical tests for water absorption and breaking strength (ASTM C 648). Additional test work was conducted in order to optimize the temperature profile and develop special measures to improve the airflow in the kiln. Statistical analysis was conducted on the data obtained by physical testing of all tiles produced in 2002—2003. It demonstrated strong correlation between shrinkage, water absorption and strength.

The potential field of the ash suppliers was extended by testing fly ash from two Ameren power plants. The tests were performed on the mixes with Ameren fly ashes: Coffeen (high carbon) and Meredosia (low carbon).

The demonstration run was conducted at the TCA test center using a commercial type hydraulic press and roller kiln. The process parameters varied throughout the consequent tests. Six firing tests were conducted, with variable firing time, rate of heating, and temperatures. By varying these parameters, satisfactory degree of the carbon removal was achieved. The tiles produced during the run were subjected to testing at TCA and in CTL labs and demonstrated conformance with the standard specifications for wall tiles. Tiles produced in this test were successfully glazed in the second firing.

The results demonstrated that commercial production of tiles using fly ash as a major raw material is technically feasible, based on the technology developed in this project. Previously, a marketing and economic study confirmed the economic feasibility of using this technology at an industrial scale. Now it appears possible to implement the technology on a commercial scale. The results of this phase will serve as a basis for the prospective development project of a commercial tile plant utilizing Illinois fly ash as a major raw material.

EXECUTIVE SUMMARY

Fly ash is the solid product of combustion of pulverized coal in power plants. The State of Illinois alone produces annually over one million tons of fly ash. Only 20% of this fly ash is utilized by the cement and concrete industry and the rest is landfilled. Therefore, any non-concrete utilization of the currently disposed fly ash would not only be environmentally sound and cost effective, but will also create a stable year-round demand.

The overall objective of this project is to utilize fly ash as the major raw ingredient for manufacturing value-added ceramics. Considering the size of the tile industry, a considerable fraction of the fly ash produced in Illinois can be utilized to prepare ceramic tiles. As raw materials constitute to the major cost in running a tile plant, replacement of costly raw materials by fly ash is attractive to tile manufacturers.

The project focused on manufacturing tiles out of fly ash at a commercial tile plant located in the State of Illinois. Therefore, most of the experimental work was conducted at the tile plant by M.E. Tile Co., an Illinois corporation. As an extension of the previous research, fly ash-based tiles were manufactured experimentally with characteristics similar to those of conventional tiles. For commercialization of this technology, the production parameters were investigated based upon the key factors for the commercial manufacturing of fly ash-based tiles. The most important obstacle encountered in experimental production of tiles from carbon-containing fly ashes was the detrimental effect of carbon on the physical integrity and appearance of the product. This problem was successfully addressed by development of the firing schedules allowing carbon oxidation in the tile mix prior to the temperature when sintering begins and seals the pores of the tile body. The current phase of the research was designed to refine the technology and test it in a commercial tile manufacturing plant.

Three separate but interrelated tasks were pursued during this phase of the project. Breaking strength and water absorption were selected as the most important criteria defining the quality and applications of ceramic tiles.

First, in order to increase the tile density without raising the firing temperature, it was suggested to increase the content of fluxes (nepheline-syenite and talc) in the mix. Fluxes can reduce the temperature when the liquid phase appears in the mix and reduce the liquid's viscosity. These effects are caused primarily by oxides of magnesium, sodium, and potassium.

Mixes identified as 02-1 and 02-2 were prepared and tested in comparison with the basic mix to provide clear indication of the effects of the fluxes on the tile quality. These mixes contained respectively, 46% and 52% of fly ash, compared with 43% in so-called basic mix (see Table 6 in the main body of the report).

Tiles made from these mixes were fired at 1119°, 1142°, and 1162°C, with 30, 60, and 90 minute hold at 700°C. The results of testing were analyzed statistically. It was established that correlation coefficients between strength and firing shrinkage and between strength

and water absorption were 0.68 and –0.56, respectively. These values are statistically significant at 2% significance level. It is important to note that all tiles were free of residual carbon. It means that the temperature profile of pre-firing for this mix was satisfactory. However, this series of tests indicated that the basic mix produced the best results, and further modifications were not warranted.

In order to extend the potential resource base, at ICCI request, additional work was performed on the use of fly ashes from Ameren Corporation. Two fly ashes were obtained from the Ameren power plants at Coffeen and Meredosia. Additional laboratory analyses (PSD, oxide analysis) were conducted for ash characterization. Chemical analysis of these ashes is given in Table 2 of the report.

Proportions of major oxides in both ashes were almost identical. However, the ashes differed drastically in the loss on ignition (LOI). To determine what portion of LOI is attributed to actual carbon content, the ashes were examined by thermogravimetric analysis (TGA). The actual fixed carbon values are included in the table.

For further testing, tiles were produced from the mixes with the Ameren fly ashes. They were fired at 1162°C with varying hold at 700°C. The ashes differed in their carbon content, which led to drastically different results. Table 8 and 9 of the report give average characteristics of the tiles made from both ashes.

As we stated, the carbon content in Meredosia ash was low, and its removal was accomplished in a relatively short hold at 700°C. Actually, longer hold was not only unnecessary but led to decreased breaking strength.

Tiles from the Coffeen ash required much longer hold at for burning out carbon and producing acceptable shape stability. However, breaking strength of these tiles remained well below that of the Meredosia batch.

The rate of carbon removal depends not only on the temperature but also on the oxygen partial pressure in the kiln gas. Atmosphere in electric kilns at M.E. Tile Co. is pure air whereas commercial and pilot roller kilns (such as at TCA test center) are gas fired, and oxygen content is substantially lower. Indeed, some decrease in the degree of carbon oxidation was detected even when a smaller electric kiln was used. It was expected that the firing profile developed for the electric kiln should be adjusted for the gas-fired kiln.

To evaluate the effect of the kiln atmosphere on the rate of carbon removal, a typical mix was examined by TGA in air and in simulated flue gas with 2.5% oxygen content. The results are briefly summarized in Table 10. It is obvious that oxidation is retarded in the flue gas environment.

Based on these observations, further tests were conducted to optimize the temperature profile with the objective of improving conditions for carbon oxidation. The principal concept was to reduce the hold temperature and to avoid premature encapsulation of carbon by emerging liquid phase. This objective was achieved after several trials.

The test work as described above laid a foundation for the demonstration run at the TCA test center. Special attention was paid to dry pressing, being the technology of choice for future commercialization. It was tested at the pilot facility closely simulating the industrial tile production environment. Processing methods and parameters that are relevant to commercialization of this technology, such as the pressing methods, temperature profiles, glaze composition, were emphasized in this program.

Raw powder of clay, fly ash, and fluxes was prepared by dry batch mixing (see Table 3). The temperature profile of a state-of-the-art roller kiln was optimized for effective carbon removal, making it possible to scale up this technology and size the kiln for commercial production. Tiles produced in the course of the experimental run met standard quality requirements.

The results of this study demonstrated that the problem of the residual carbon could be resolved. In our tests the high proportions of fly ash (over 50%) were shown to be used without any detrimental effects in commercial manufacturing of ceramic tiles using wet pressing, slip casting, and dry pressing methods. The causes of a few problems relevant to processing and appearance have been identified, and remedial measures developed. The test results indicate that characteristics of fly ash-based tiles are superior to those required for wall tile applications and approaching those required for floor and outdoor applications. Several fly ash tile bodies have also passed the standard specifications used in the tile industry, indicating potential for floor and outdoor applications.

OBJECTIVES

The overall objective of the project is to offer the technology utilizing fly ash produced by burning Illinois coal as a major raw ingredient to manufacture ceramic tiles, and to commercialize the technology.

For the producers and users of Illinois coal, a number of economic benefits are associated with the manufacturing of ceramic tiles using fly ash that is currently landfilled. In addition to being environmentally friendly, this technology will generate additional revenue through marketing this value-added product.

In the previous phases of this program a method was developed to minimize the effect of residual carbon in fly ash on the product quality. In the most recent stage of the project, efforts concentrated on optimization of the mix compositions. The objective of the current project was to conclude the experimental work with a demonstration run using the typical equipment simulating the future commercial pressing and firing processes.

INTRODUCTION AND BACKGROUND

In the previous phases of this program a number of mixes of fly ash with clay and other conventional raw materials were tested in experimental tile manufacture. Residual carbon in fly ash was identified as the principal source of the tile warping and bloating in firing. A processing method has been developed to minimize the effect of compositional variability of fly ash on the product quality. The salient feature of this method was the firing temperature profile which provided for almost complete carbon removal prior to sintering. In addition, it was shown that to achieve comparable physical characteristics of commercial tiles, fly ash tiles require lower firing temperatures. Based on this method, ceramic tiles from mix containing about 50% of fly ash were made at a commercial tile manufacturing plant in Illinois by wet pressing. Based on the produced results, an experimental run was conducted at a larger scale using the typical commercial dry-pressing plant equipment. It was confirmed that the proper selection of the firing temperature profile provides for the satisfactory degree removal of residual carbon. The principal quality characteristics of the tiles, breaking strength and water absorption, met the standard requirements for wall tiles.

Simultaneously, a marketing and economic study confirmed the feasibility of using this technology at the industrial scale.

For the acceptance of this technology by the ceramic tile industry, it was deemed desirable to bring the tile quality up to the more demanding floor tile specifications. This required an additional although limited scope of experimental batch production. Finally, the project was concluded by producing tiles in a continuous operation at a facility fully simulating the future commercial production process.

The proposed program brought the technology of manufacturing ceramic tiles using high dosages of fly ash to a continuously operated production line. A commercial tile manufacturer of Illinois was actively participating in this program, along with the selected test facility.

EXPERIMENTAL PROCEDURES

1. Testing of Modified Mix Compositions.

Most physical characteristics of tiles can be improved with the increase of the tile body density. In order to increase this without increasing the firing temperature, it was suggested to increase the content of fluxes (nepheline-syenite and talc) in the mix.

Fluxes can reduce the temperature when liquid phase appears in the mix and reduce the liquid's viscosity. These effects are caused primarily by the presence of oxides of magnesium, sodium, and potassium.

Table 1 shows chemical composition of the mix ingredients.

Table 1. Chemical composition of the principal materials (% by wt.)

Raw materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Ball clay	57.6	27.5	1.1	0.2	0.4	1.5	0.2	10.3
Fly ash	51.7	23.5	9.4	4.7	1.1	1.7	2.3	3.3
Nepheline	44.0	33.2				15.1	7.7	
Talc	63.5				34.1			4.8
Wollastonite	51.7			48.3				

Based on the chemical composition of mix compositions, several hypothetical mixes were designed. The potential effect of the composition variations on liquid phase formation was analyzed by means of phase diagrams.

After the mix compositions were selected, tiles made from these mixes were fired at 1119°, 1142°, and 1162°C, with 30, 60, and 90 minute hold at 700°C.

Tiles were measured for the determination of drying shrinkage, tested for water absorption, and breaking strength (ASTM C 648) using the standard test apparatus fabricated at CTL for this purpose. The results of testing were analyzed statistically.

2. Investigation of Alternate Fly Ashes

In order to extend the potential resource base, ICCI requested additional work using fly ashes from Ameren Corporation. Two fly ashes were obtained from the Ameren power plants at Coffeen and Meredosia. Additional laboratory analyses (PSD, oxide analysis) were conducted for the ash characterization.

Chemical analysis of these ashes is given in Table 2 (in comparison with Vermillion ash used in most of previous tests) as well as in the Appendix.

Table 2. Chemical composition of fly ashes (% by wt.)

	Vermillion	Coffeen	Meredosia
SiO_2	46.65	46.51	53.87
Al_2O_3	21.52	17.39	19.47
Fe_2O_3	12.39	7.73	10.55
CaO	4.73	4.12	4.83
MgO	1.07	1.20	1.15
SO_3	0.68	0.66	0.68
Na_2O	1.73	2.01	1.55
K_2O	2.32	2.71	2.39
TiO_2	1.00	1.10	1.01
P_2O_5	0.19	0.20	0.21
Mn_2O_3	0.04	0.04	0.06
SrO	0.05	0.06	0.06
Cr_2O_3	0.03	0.03	0.03
ZnO	0.10	0.11	0.07
LOI (950^{o}C)	8.50	15.08	3.58
Fixed carbon (TGA)	6.32	11.34	1.63

Proportions of major oxides in both ashes were almost identical. However, the ashes differed drastically in the loss on ignition (LOI). To determine what portion of LOI is attributed to actual carbon content, the ashes were examined by thermogravimetric analysis (TGA). The fixed carbon values are included in Table 2.

Tiles were produced from the basic mix wherein Vermillion ash was replaced by Coffeen and Meredosia ashes. The tests followed the same procedures as those described earlier in this report.

3. Optimization of the Temperature Profile

The higher carbon content of some ashes raised another question related to the carbon removal. The rate of oxidation depends not only on the temperature but also on the oxygen concentration. Atmosphere in electric kilns at M.E. Tile Co. is pure air whereas commercial and pilot roller kilns (such as at TCA test center) are gas-fired, and oxygen content in the kiln gas is substantially lower. Indeed, some decrease in the degree of carbon oxidation was detected even when an electric kiln with smaller internal volume was used. It was expected that the firing profile developed for the electric kiln should be adjusted for the gas-fired kiln.

To evaluate the effect of the kiln atmosphere on the rate of carbon removal, a typical mix was examined by TGA in air and in simulated flue gas with 2.5% oxygen content.

Based on these observations, further tests were conducted to optimize the temperature profile with the objective of improving conditions for carbon oxidation. The principal

concept was to reduce the hold temperature and to avoid premature encapsulation of carbon by emerging liquid phase. This objective was achieved after several trials.

4. Demonstration Tests at TCA Test Facility

Tests at the research facility of the Tile Council of North America (TCA), Anderson, South Carolina, were conducted on April 5 through 8, 2004. The mix in the amount of about 900 lbs was prepared at M.E. Tile Co. by blending the ingredients in a Mueller mixer. The mix proportions are given in Table 3.

Table 3. Dry mix for pilot testing

Raw materials	% by wt.
Ball clay	38.0
Fly ash	43.0
Nepheline	12.0
Talc	3.0
Wollastonite	4.0

The TCA facility operates two core pieces of tile-making equipment, a hydraulic press and a roller kiln. The hydraulic press by WELKO (Italy) is a commercial model with maximum load of 650 tonnes (Fig. 1).

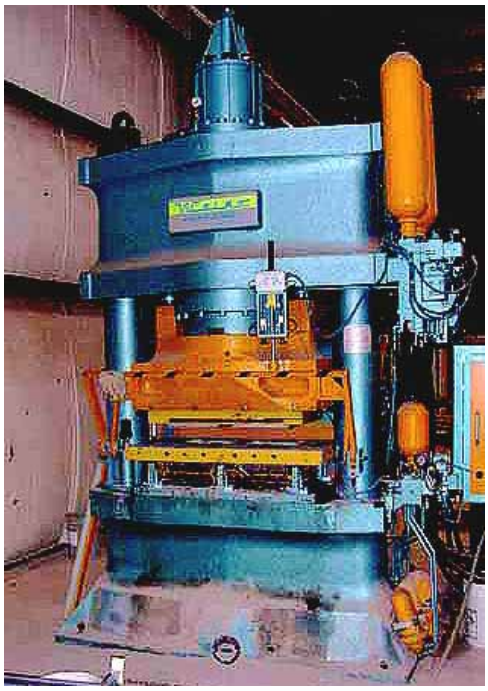

Fig. 1. WELCO hydraulic press

The kiln by Studio Uno (Italy) is a shortened version of a commercial kiln (Figs. 2 and 3). It consists of 9 sections, each 2 meters long (total length 18 m, or 60 ft).

Fig 2. Firing zone of the kiln

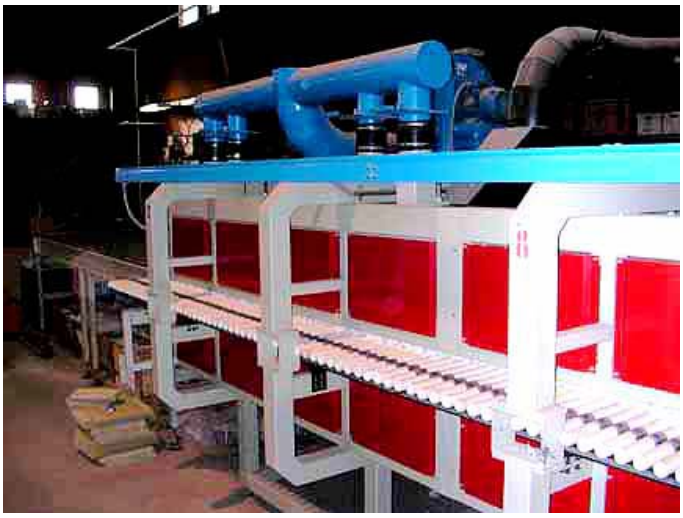

Fig. 3. Cooling zone of the kiln

Tiles are supported and conveyed through the kiln by a system of rotating rollers. The rollers are driven by five separate independently controlled drives. Gas burners are installed in five sections below and above the level of rollers. Temperature in each section is controlled automatically.

Prior to the tests, the press was outfitted with a mechanical feeder and a feed bin. Additional adjustment work was conducted on the kiln by a Studio Uno technician. The green tiles were oven dried and loaded into the kiln.

Following are the principal process parameters of the test.

- Tile size: 300x300 mm (12”x12”)
- Thickness: 7.1 mm to 8.7 mm ($^{9}/_{32}$” to $^{11}/_{32}$”)
- Moisture: 7.5 to 10%
- Pressure: 120 to 160 kg/cm^2
- Six (6) tests were conducted in different firing cycles

The following parameters varied during the test: mix moisture; mold pressure; kiln temperature profile controlled by the speed of each of 5 drives and temperature settings of 5 burner sections. Dry mix with added by weight water was prepared in an Eirich batch blender.

The pressure regimens varied throughout the consequent tests. During the pressing cycle, the powder fills the cavity of the mold and is subjected first to relatively low pressure to de-aerate the future tile body. Subsequently, the second pressing is applied which forms the green tile suitable for further processing. In our tests each batch slated for firing was subdivided into three sub-batches, with second pressing at 140 bar, 130 bar, and 120 bar, identified as pressure 1, 2, and 3, respectively.

Spreadsheets detailing the parameters of each test are given in the Appendix.

RESULTS AND DISCUSSION

Task 1. Testing of Modified Mix Compositions.

Several hypothetical mixes were designed to represent variable oxide proportions, based on the chemical composition of mix ingredients. Tables 4 and 5 illustrate the modification of the mix chemical composition by fluxes. Mix A represents the basic mix. Mixes B through E have varying proportions of fly ash, nepheline, and talc.

Table 4. Composition of trial mixes (% by wt.)

Raw materials	A	B	C	D	E
Ball clay	38.0	38.0	38.0	38.0	38.0
Fly ash	43.0	36.5	43.0	48.0	48.0
Nepheline	12.0	17.0	7.5		5.0
Talc	3.0	4.5	7.5	10.0	5.0
Wollastonite	4.0	4.0	4.0	4.0	4.0

The corresponding chemical compositions of the mixes are shown in Table 5.

Table 5. Chemical composition of the mixes (% by wt.)

Blends (as is)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
A	53.3	24.6	4.5	4.0	1.6	3.1	2.0	5.5
B	53.1	24.7	3.8	3.7	2.1	3.8	2.2	5.3
C	54.2	23.1	4.5	4.0	3.2	2.4	1.6	5.7
D	55.1	21.7	4.9	4.3	4.1	1.4	1.2	6.0
E	54.1	23.4	4.9	4.3	2.4	2.2	1.6	5.8

The potential effect of the composition variations on liquid phase formation was analyzed by means of phase diagrams. It was concluded that the following mixes identified as 02-1 and 02-2 should be prepared and tested in comparison with the basic mix to provide clear indication of the effects of fluxes on the tile quality (Table 6).

Table 6. Composition of test mixes (% by wt.)

	02-1	02-2
Fly ash	46	52
Clay KTI-4	38	38
Wollastonite	4	4
Talc	6	6
Nepheline-syenite	6	0
Bentonite	2	2

Tiles made from these mixes were fired at 1119°, 1142°, and 1162°C, with 30, 60, and 90

minute hold at 700°C.

Tiles were measured for the determination of drying shrinkage, tested for water absorption, and breaking strength (ASTM C 648) using the standard test apparatus fabricated at CTL for this purpose. It is important to note that all tiles were free of residual carbon. It means that the temperature profile of pre-firing for this mix was satisfactory.

All test data are summarized in Table 7. Statistical analysis demonstrated strong correlation between shrinkage, water absorption and strength.

Table 7. Summary of physical testing: average results

Mix	Temperature, °C	Hold, min.	Breaking strength, lb	Shrinkage, %	Water abs.,%
Basic	1142	30	160	8.25	7.7
Basic	1142	60	171	8.44	7.5
Basic	1142	90	176	8.30	7.3
Basic	1162	30	273	9.47	
Basic	1162	60	252	9.50	
Basic	1162	90	273	9.68	
02-1	1142	30	126	7.22	13.1
02-1	1142	60		7.79	
02-1	1142	90	159	7.68	11.7
02-1	1154	60	157	6.54	10.4
02-1	1158	30	158		8.5
02-1	1162	30		8.03	
02-1	1162	60	142	8.09	8.8
02-1	1162	90	168	10.64	1.8
02-2	1142	30	130	6.38	12.3
02-2	1142	60		6.49	
02-2	1142	90	145	6.11	13.1
02-2	1154	60	138	6.54	12.4
02-2	1158	30	150		10.3
02-2	1162	30		6.86	
02-2	1162	60	137	7.13	9.8
02-2	1162	90	128	8.11	7.0

The results of testing were analyzed statistically. It was established that correlation coefficients between strength and firing shrinkage and between strength and water absorption were 0.68 and -0.56, respectively. These values are statistically significant at 2% significance level.

The series of tests described in this section indicated that the basic mix produced the best results, and further modifications were not warranted.

Task 2. Investigation of Alternate Fly Ashes

For testing fly ashes from alternate sources, tiles were produced from the mixes with the Ameren fly ashes. They were fired at 1162°C with varying hold at 700°C and tested according to the usual procedures. The ashes differed in their carbon content (see Table 2), which led to drastically different results. Table 8 gives average characteristics of tiles produced from the mixes with Meredosia ash.

Table 8. Tiles with Meredosia ash

Hold at 700°C, min.	Shrinkage, %	Water absorption, %	Break strength, lbs
0	10.33	1.3	115
30	10.29	0.8	149
90	10.25	0.6	115

As we stated, the amount of carbon in Meredosia ash was low, and its removal was accomplished by a relatively short hold at 700°C. Actually, longer hold was not only unnecessary but led to the decreased breaking strength.

Tiles from the Coffeen ash required much longer hold at for burning out carbon and producing acceptable shape stability. However, breaking strength of these tiles remained well below that of the Meredosia batch (Table 9).

Table 9. Tiles with Coffeen ash

Hold at 700°C, min.	Shrinkage, %	Water absorption, %	Break strength, lbs
30	9.62	0.4	106
90	10.03	0.2	113

These results necessitated further investigation of the effects of the firing regimen on the rate and degree of carbon oxidation.

Task 3. Optimization of the Temperature Profile

To further evaluate the effect of the kiln conditions on the rate of carbon removal, a typical mix was examined by TGA in air and in simulated flue gas with 2.5% oxygen content. The results are briefly summarized in Table 10 (the actual TGA chart is given in the Appendix).

Table 10. Distribution of weight losses, %, by temperature ranges

	Temperature range, °C	In air	In flue gas
1	50 – 330	0.65	0.46
2	330 – 620	3.21	2.88
3	620 – 700	1.78	1.48
4	700 – 800	0.16	0.25
Total	50 – 800	5.81	5.05

It is evident that oxidation is retarded in the flue gas environment. For obvious reasons, only in the 700° to 800° range the weight loss in flue gas is higher than in air, but the total loss does not reach the same value as in air. These results correlate well with the results of tests at M.E. Tile Co.

Based on these observations, further tests were conducted to optimize the temperature profile with the objective of improving conditions for carbon oxidation. The principal concept was to reduce the hold temperature and to avoid premature encapsulation of carbon by emerging liquid phase. This objective was achieved after several trials. The optimized temperature profile is presented below (Fig. 4).

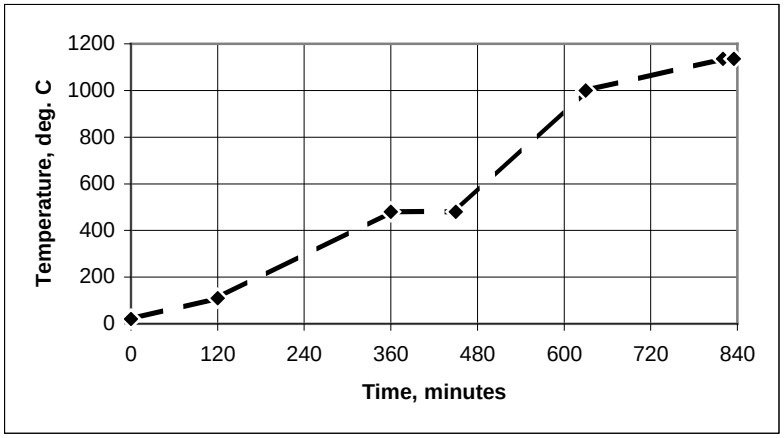

Fig. 4. Optimized temperature profile for batch firing

The physical test results of the tiles produced under this regimen are given in Table 11.

Table 11. Physical properties of tiles (optimized firing)

	Coffeen		Meredosia	
	Water abs.%	Break.strength, psi	Water abs.%	Break. strength, psi
1	0.2	175	0.2	210
2	0.2	135	0.3	100
3	0.2	140	0.5	180
4	0.1	165	0.7	130
5	0.2	100	0.1	200
Average	0.2	143	0.3	164

Task 4. Demonstration Tests at TCA Test Facility

The clay mix (see Table 3) prepared at M.E. Tile Co. was used for manufacturing tiles at the TCA test facility. The tile size was 300x300 mm (12”x12”), with thicknesses 7.1 mm to 8.7 mm ($^{9}/_{32}$” to $^{11}/_{32}$”). The mix was mixed with water in an Eirich batch blender to achieve the total moisture of 7.5 to 10%. The mold pressure varied from 120 to 160 kg/cm^2.

Both moisture and pressure are critical for forming a green tile body that is sufficiently strong for further handling. At the same time, they both should provide conditions for de-aeration of the powder, to avoid air entrapment would cause the body delamination. Moisture also affects the green tile permeability, which in turn may affect carbon oxidation. After several trials is was established that 8% moisture gives the best results.

The pressure regimens varied throughout the consequent tests. During the pressing cycle, the powder fills the cavity of the mold and is subjected first to relatively low pressure to de-aerate the future tile body. Subsequently, the second pressing is applied which forms the green tile suitable for further processing. In our tests each batch slated for firing was subdivided into three sub-batches, with second pressing at 140 bar, 130 bar, and 120 bar, identified as pressure 1, 2, and 3, respectively.

Firing temperature is the most important process parameter. Six (6) tests were conducted in different firing cycles. The kiln temperature profile was controlled by the speed of each of 5 drives and temperature settings of 5 burner sections. Following is a brief description of the test parameters.

- **Cycle 1.** One-step cycle, 83 minute long, with about 20 minute hold at 700–800°C, final firing temperature 1120°C.
- **Cycle 2**. Pre-firing cycle, 111 minute long, with about 30 minute hold at 500°C, final temperature 800°C.
- **Cycle 3**. Firing cycle (using bisque produced in Test 2), 52 minute long, final firing temperature 1125°C.
- **Cycle 4**. Pre-firing cycle, 108 minute long, with about 30 minute hold at 500°C, final temperature 800°C, similar to Test 2.
- **Cycle 5**. Firing cycle (using bisque produced in Test 4), 52 minute long, final firing temperature 1163°C, similar to Test 3, but with more rapid heating rate and higher final temperature.
- **Cycle 6**. Firing cycle (using bisque produced in Test 4), 54 minute long, final firing temperature 1122°C.

Spreadsheets detailing the parameters of each test are given in the Appendix. The temperature profiles of these cycles are shown graphically on Figures 5 and 6.

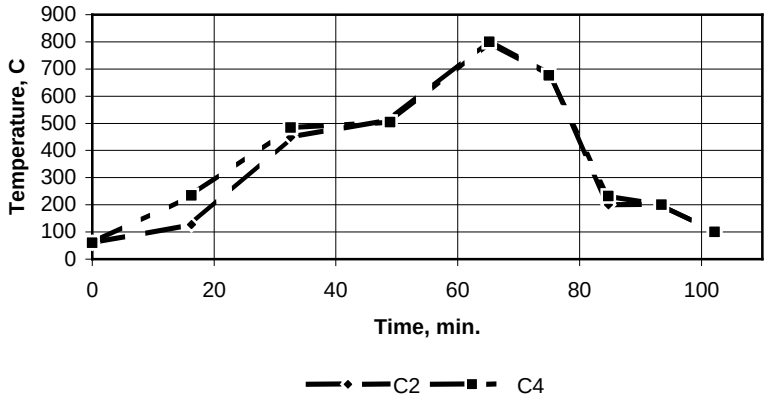

Fig. 5. Temperature profiles of pre-firing cycles.

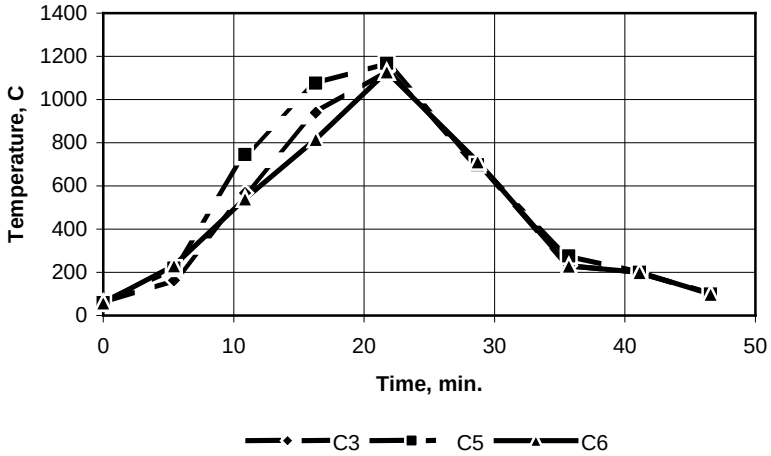

Fig. 6. Temperature profiles of firing cycles.

As was expected, the relatively short firing schedule in Test 1 produced tiles with massive carbon core, characteristically bloated and warped. Three batches slated for testing were produced in Cycles 2+3, 4+5, and 4+6 (identified in testing as Runs 1, 2, and 3, respectively). Within each batch, second pressing was varied from 120 bar to 140 bar.

Visual inspection showed that in Run 2 accelerated heating and higher firing temperature caused intensive bloating, but in Runs 1 and 3, the tiles produced were fully acceptable, with flat surfaces and no visible discoloration. Fractures of tiles from Run 1 showed a layer of residual carbon. Run 3, with modified heating rates and hold periods produced

better results, and the tiles contained virtually no carbon. The results of physical testing of tiles from Runs 1 and 3 are shown in Table 12.

Table 12. Physical testing of tiles produced at TCA

		Water absorption, %	Breaking strength, lbs
ANSI A137.1	Wall tiles	<20	90
	Floor tiles	<7	250
Run 1	Low pressure	16.4	162
	High pressure	15.1	181
Run 3	Low pressure	17.1	143
	High pressure	14.6	199

It is evident that strength and water absorption was significantly affected not only by the relatively small variations of the firing conditions, but also by the pressure during the second part of the pressing cycle. Higher pressure resulted in higher breaking strength and lower water absorption, although lower pressure was somewhat more efficient in facilitating carbon removal. The best tiles had average strength of 199 lbs and water absorption about 14%. This far exceeds the standard specifications for wall tiles.

The overall objective of this project was preparation of the technical basis for commercial-scale ceramic tile manufacturing utilizing sizable amounts of fly ash. Experimental work described in this report largely accomplished this task. Tests at the small-scale production equipment demonstrated the reliable way to remove residual carbon from the mixes by carefully designed set of firing conditions. The mix compositions were finalized. Demonstration run at the commercial type equipment confirmed the process approach developed on a smaller scale. By varying key process parameters, such as pressing and temperature profiles, it was proven feasible to produce tiles of acceptable quality, meeting the standard requirements. The results of this stage of the investigation lead directly to the possibility of designing and operating a commercial tile manufacturing facility utilizing Illinois-generated fly ash.

The next step in implementation of the technology developed within the framework of this project (manufacturing of ceramic tiles utilizing high dosages of Illinois fly ash) would be construction of the tile manufacturing plants. However, some unanswered questions still have to be addressed. Modern tile plants use continuous preparation of the mix in a form of pourable suspension (slip) followed by spray drying. Therefore, some additional test work is still needed to evaluate the behavior of ash-containing slips in the powder preparation equipment. The specific ashes produced physically close to the location of the future manufacturing facility should be tested. This testing will also provide an opportunity to reduce he tile water absorption and increase strength in order to meet requirements for floor tiles that constitute a substantially larger market segment.

Since the future demonstration plant should incorporate wet blending and spray drying as the most common mix preparation technology in the tile industry, slips for testing should be prepared and spray-dried in the commercial equipment. This will enable to assess rheological behavior of ash-containing suspensions, determine the necessary water

content of the slip and operation parameters of the spray dryer. Suitable venues for this testing should be found.

Mix preparation process may lead to modifications of the raw mix. This may in turn lead to changes in sintering behavior of green tiles. Therefore, some test work should be done to balance these requirements without excessively high firing temperatures. An improved mix composition may also reduce water absorption of the tiles. This is important from the marketing standpoint, since favorable water absorption results will make the tiles suitable for floor tile application, which is in greater demand than wall tile.

Summarizing these conclusions, it may be stated that the next phase of the investigation should include:

(a) quantification of the principal parameters of the production process using fly ash to manufacture tiles;

(b) assessment of the supply and cost of raw materials, cost of equipment, design of production plant, cost of building such a facility, and costs of operation.

CONCLUSIONS AND RECOMMENDATIONS

- Presence of residual carbon in fly ash is the principal obstacle in use of fly ash for tile manufacturing.

- Studies at the laboratory and small-production scales demonstrated that residual carbon could be removed from the formed tile bodies by oxidation in kilns with carefully selected firing schedule.

- The composition of raw mixes affects significantly physical characteristics of tiles and parameters of the manufacturing process.

- Experimental work wherein the mix proportions and source of fly ash varied resulted in the development of optimized mixes suitable for pilot production.

- Experimental runs using commercial-type production equipment, including dry pressing and firing in a roller kiln, demonstrated that wall tiles meeting the standard requirements can be produces from mixes with over 40% of fly ash with substantial carbon content.

- The results of this project can be utilized as the basis for large-scale industrial tile production with fly ash as a major mix ingredient.

- Additional experimental work is required to resolve some issues related to wet mix preparation and drying.

DISCLAIMER

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APPENDIX

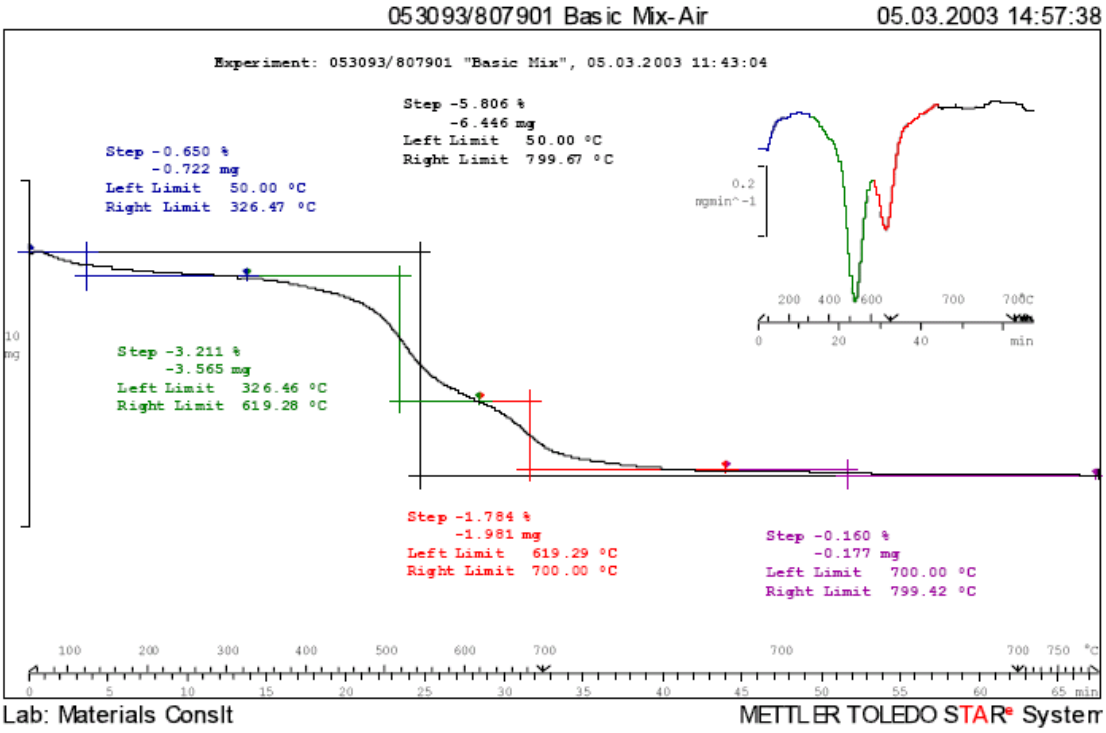
1. Chemical analysis of fly ashes

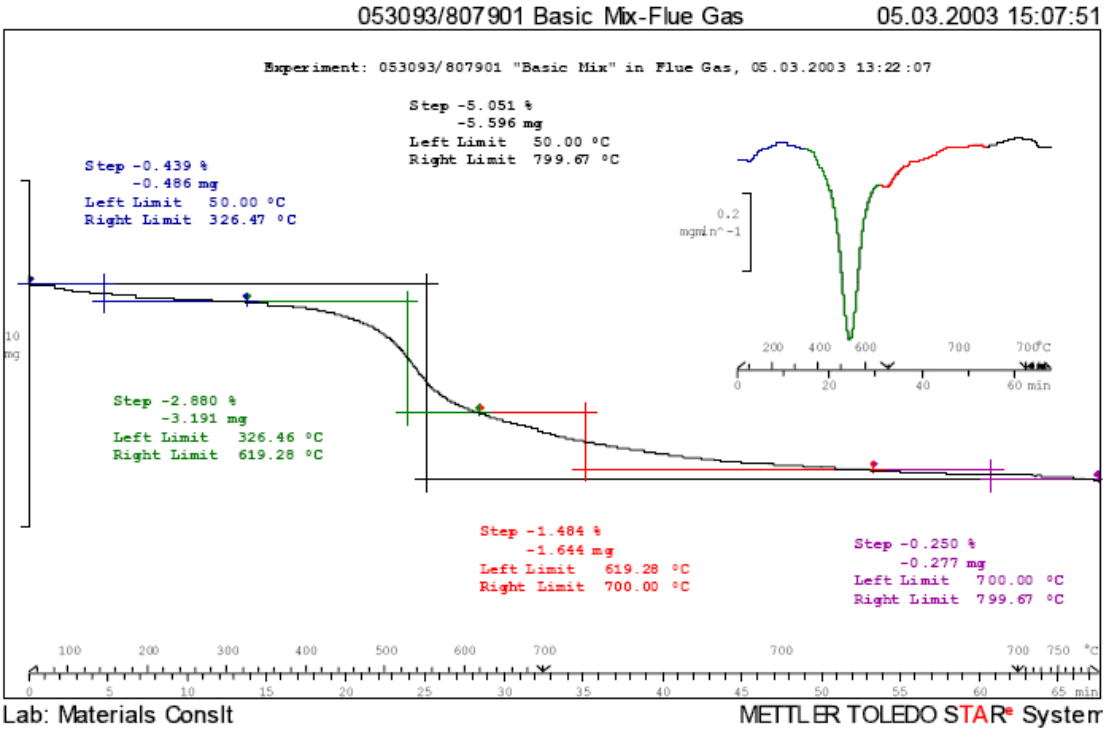
Client:	**Illinois Clean Coal Institute**	CTL Project No.:	**053093**
Project:	**Chemical Analysis**	CTL Proj. Mgr.:	**Alex Mishulovich**
Contact:	**Ron Carty**	Approved:	
Submitter:	**Alex Mishulovich, CTL**	Date Analyzed:	**29-May-03**
Date Rec'd:	**27-May-03**	Date Reported:	**11-Jun-03**

REPORT OF CHEMICAL ANALYSIS

Client's Sample ID:	Coffeen	Meredosia
Material type:	Fly ash	Fly ash
CTL Sample ID:	867301	867302
Analyte	Weight %	Weight %
SiO_2	46.51	53.87
Al_2O_3	17.39	19.47
Fe_2O_3	7.73	10.55
CaO	4.12	4.83
MgO	1.20	1.15
SO_3	0.66	0.68
Na_2O	2.01	1.55
K_2O	2.71	2.39
TiO_2	1.10	1.01
P_2O_5	0.20	0.21
Mn_2O_3	0.04	0.06
SrO	0.06	0.06
Cr_2O_3	0.03	0.03
ZnO	0.11	0.07
LOI (950^oC)	15.08	3.58
Total	98.97	99.51
Alkalies as Na_2O	3.80	3.13
Moisture	0.34	0.13
$SiO_2+Al_2O_3+Fe_2O_3$	71.62	83.89

2. TGA Analysis of High-Carbon Ash





3. Demonstration tests at the TCA test center, Anderson, SC

Test:	**1**	**2004**

Press Dept:				
Mould size:	315.54	X	315.54	
Cavities:	2			
Powder moisture:	8%			
First pressing:	140	Bar	64.75	Kg/cm2
Second pressing:	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	25.09	1	9.74	60	60
		2	9.74	103	294
2	25.04	3	9.76	658	658
		4	9.76	813	735
3	28.06	5	8.71	1120	1141
		6	8.71	652	756
4	28.06	7	8.71	310	94
		8	8.71	200	200
5	28.06	9	8.71	100	100

82.57	Minutes
1.38	Hrs

Firing Chart:

BISC ONLY

Test: 2 2004

Press Dept:

Mould size:		315.54	X	315.54	
Cavities:		2			
Powder moisture:		8%			
First pressing:		140	Bar	64.75	Kg/cm2
Second pressing:	TEST 1	140	Bar	259.00	Kg/cm2
	TEST 2	130	Bar	240.50	Kg/cm2
	TEST 3	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	15.00	1	16.30	60	60
		2	16.30	76	178
2	15.00	3	16.30	437	461
		4	16.30	548	480
3	25.00	5	9.78	813	800
		6	9.78	651	711
4	28.02	7	8.72	314	87
		8	8.72	200	200
5	28.06	9	8.71	100	100

110.90	Minutes
1.85	Hrs

FIRING ONLY

Test: 3 2004

Press Dept:

Mould size:		315.54	X	315.54	
Cavities:		2			
Powder moisture:		8%			
First pressing:		140	Bar	64.75	Kg/cm2
Second pressing:	TEST 1	140	Bar	259.00	Kg/cm2
	TEST 2	130	Bar	240.50	Kg/cm2
	TEST 3	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	45.00	1	5.43	60	60
		2	5.43	**95**	**231**
2	45.00	3	5.43	**568**	**566**
		4	5.43	**949**	**931**
3	35.00	5	6.98	**1125**	**1145**
		6	6.98	**650**	**735**
4	45.00	7	5.43	**349**	**113**
		8	5.43	200	200
5	45.00	9	5.43	100	100

51.99	Minutes
0.87	Hrs

BISC ONLY

Test: 4 2004

Press Dept:

Mould size:		315.54	X	315.54	
Cavities:		2			
Powder moisture:		8%			
First pressing:		140	Bar	64.75	Kg/cm2
Second pressing:	TEST 1	140	Bar	259.00	Kg/cm2
	TEST 2	130	Bar	240.50	Kg/cm2
	TEST 3	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	15.00	1	16.30	60	60
		2	16.30	**93**	**375**
2	15.00	3	16.30	**497**	**471**
		4	16.30	**547**	**461**
3	25.00	5	9.78	**799**	**800**
		6	9.78	**650**	**702**
4	28.02	7	8.72	**350**	**114**
		8	8.72	200	200
5	45.00	9	5.43	100	100

107.62	Minutes
1.79	Hrs

FIRING ONLY

Test: 5 2004

Press Dept:

Mould size:		315.54	X	315.54	
Cavities:		2			
Powder moisture:		8%			
First pressing:		140	Bar	64.75	Kg/cm2
Second pressing:	TEST 1	140	Bar	259.00	Kg/cm2
	TEST 2	130	Bar	240.50	Kg/cm2
	TEST 3	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	45.00	1	5.43	60	60
		2	5.43	**111**	**329**
2	45.00	3	5.43	**765**	**725**
		4	5.43	**1086**	**1064**
3	35.00	5	6.98	**1163**	**1172**
		6	6.98	**653**	**744**
4	45.00	7	5.43	**395**	**155**
		8	5.43	200	200
5	45.00	9	5.43	100	100

51.99	Minutes
0.87	Hrs

FIRING ONLY

Test: 6 2004

Press Dept:

Mould size:		315.54	X	315.54	
Cavities:		2			
Powder moisture:		8%			
First pressing:		140	Bar	64.75	Kg/cm2
Second pressing:	TEST 1	140	Bar	259.00	Kg/cm2
	TEST 2	130	Bar	240.50	Kg/cm2
	TEST 3	120	Bar	222.00	Kg/cm2

Kiln Dept:

Drives	Inverter Hz	Kiln Sect.	Cycle /min.	Upper Temperatures	Lower Temperatures
1	40.00	1	6.11	60	60
		2	6.11	**88**	**374**
2	40.00	3	6.11	**535**	**547**
		4	6.11	**835**	**798**
3	40.00	5	6.11	**1122**	**1135**
		6	6.11	**651**	**774**
4	43.00	7	5.68	**335**	**125**
		8	5.68	200	200
5	43.00	9	5.68	100	100

53.72	Minutes
0.90	Hrs