FINAL TECHNICAL REPORT
September 1, 2004, through March 31, 2006

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

ICCI Project Number: 04-1/4.1B-2
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ABSTRACT

Experimental work in this project concentrated on finalization of the technical characteristics of the proposed technology, including mix composition and process parameters of spray-drying, dry pressing, and firing.

Further refinements of the technology were developed. The first task of the investigation was aimed at the increase of the tile body density without a temperature increase. Several modified mix compositions were tested, along with the optimized firing temperature profile.

Another task was related to spray drying. Fly ash-based slip demanded much higher water addition than conventional clay slips. In order to reduce the slip moisture at the given flowability, a number of chemical admixtures in different dosages were tested. This allowed reducing the water content from over 100% to about 50% (on the dry basis).

Pilot-scale testing was conducted at the American Restoration commercial type spray dryer in order to verify its operational parameters on the ash-containing slip. Finally, a demonstration run was made at the TCNA research center with spray-dried mix, using the hydraulic press and roller kiln. The tiles produced during the run were subjected to testing at TCNA and in CTL labs and demonstrated improvements in quality as compared to previous demo runs.

The previous results confirmed that commercial production of tiles utilizing fly ash as a major raw material was technically feasible. The current phase of the project completed the experimental work and provided the necessary foundation for a commercial-size production facility. Previously, a marketing and economic study confirmed the economic feasibility of using this technology at an industrial scale. The results of this phase can 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 a limited amount 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 ultimate objective of this project is to utilize fly ash as the major raw ingredient for manufacturing value-added product, namely, ceramic tiles. Depending on 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 most important obstacle encountered in experimental production of tiles from fly ashes was the presence of residual carbon and its detrimental effect on the physical integrity and appearance of the product. In the previous phases of the research, this problem was successfully addressed by development of the firing schedules allowing carbon oxidation in the tile mix prior to the point when sintering begins and seals the pores of the tile body. The current phase included testing of an alternative process of removal of high carbon content by pre-oxidation. Ultimately the work program was designed to refine the technology and test it in the equipment typical for a commercial tile manufacturing plant.

From the onset, the project focused on manufacturing tiles out of fly ash at a commercial tile plant located in the State of Illinois. Therefore, M.E. Tile Co., an Illinois corporation, has been the major partner throughout the duration of the work and conducted the bulk of the original experimental work. Later experimental work was also conducted at pilot facilities outside of the state. Fly ash-based tiles were manufactured with characteristics similar to those of conventional tiles. Key production parameters required for commercialization of this technology were projected for the prospective commercial manufacturing plant.

The program for years 2004 – 2006 built up on the progress made in the previous stages of the project. Its objective was to fully prepare the technology transfer to a demonstration or commercial facility employing typical processes, such as wet mix preparation and spray drying, common in the modern tile industry.

The previous work on this technology was based on pilot-scale production, and the mixes were prepared by dry blending. Mass production of floor and wall tiles uses currently wet mix preparation and dry pressing. Therefore, some additional test work was still needed to evaluate the behavior of ash-containing slips in the powder preparation equipment.

In order to achieve the objectives of this phase of the project, some additional developmental work was deemed necessary. This work focused on the following tasks:

1. Adjustment of the mix characteristics and firing temperature profiles in order to meet all strength and density standard specifications for both wall and floor tiles.

2. Investigation of wet preparation of the ash-containing mixes, properties of slips, spray-dryer operation, and powder behavior in pressing

This objective was accomplished by additional test work at M.E. Tile Co. (a commercial tile manufacturer, an Illinois corporation), assisted by laboratory testing at CTL. In the course of the program, experimental batches of tiles were produced and tested. The test program also used commercial-type equipment: slip preparation and spray drying at American Restoration Tile Co., Little Rock, AR, and dry pressing equipment and the roller kiln at the Tile Council of America pilot facility, Anderson, SC. This allowed to finalize the process parameters of drying, pressing, and temperature profiles of the kiln process.

In October, 2004 a batch of fly ash from Vermillion power plant was procured and subjected to laboratory analyses. Carbon content was determined by two-step TGA. It was somewhat lower than in the batch used in the previous work.

However, we also had to consider a possibility of using fly ashes with higher carbon content. In order to investigate their potential use, we studied carbon removal from virgin ash by pre-firing ash in electric furnaces at M.E. Tile facility. Batches of ash were loaded on stainless-steel trays and heated at 1300°F over the period of 90 minutes. After treatment, samples were taken from the top and bottom ¼ inch of the layer. Analysis of the samples by TGA showed that carbon content was reduced to less than 0.1%. In other words, carbon could be removed in the sufficient degree by oxidizing thermal treatment.

Pre-oxidized ash was tested in mixes with clay KT-1. The rest of the mix consisted of wollastonite, talk, nepheline-syenite, and bentonite. Tiles were fired at variable temperatures, with and without one-hour hold at 700°. This test showed that, using mixes with pre-oxidized ash at firing temperatures over 1180°C, hold is not necessary since it does not further reduce the tile water absorption.

The results of this study have demonstrated that the problem of the residual carbon could be resolved by two different or complementary methods. Carefully designed temperature profile can produce sound tile bodies from mixes with moderate amount of carbon. With higher carbon content pre-oxidation may prove more efficient thus expanding the field of usable ash sources. In our tests the high proportions of fly ash (up to 50%) were used without any detrimental effects in commercial manufacturing of ceramic tiles.

The next batch of tiles was prepared in order to evaluate effects of increased flux content on the firing temperature and tile characteristics. Four mixes were prepared in order to evaluate effects of the content of fluxes (talc, nepheline-syenite, frit) on the firing temperature and tile appearance. The mix composition is shown in the following table.

Tiles were fired at 1149°C, 1161°C, and 1185°C and tested for water absorption. The water absorption tests demonstrated that addition of frit could reduce the firing temperature by about 20°C. Increase of the nepheline-syenite content was less effective.

The entirely new direction of the investigation of wet mix preparation, which had not been addressed in the previous studies, was evaluation of the slip properties. It was established early in the experimental work that ash-based slip requires much higher water content than clay slip of the same viscosity. This necessitated testing of several water-reducing agents to achieve sufficient flowability. Tests at M.E. Tile covered 28 sets of material with up to 8 variations of composition in each set.

The fly ash was used in 3 forms: virgin fly ash, washed fly ash, and washed and demagnetized fly ash. Using barium carbonate, soda ash, and Darvon as deflocculants, usable slip was produced with 51% moisture (dry basis).

This enabled to intensify the spray dryer operation at the facilities of American Restoration Tile Co. (ART) in Little Rock, Arkansas. The ART dryer 1C-SC/100/UP by ICF-Industrie Cibec S.P.A., Italy, has evaporative capacity of 120 liters/hour. The combination of water-reducing agents allowed to increase the production capacity of the dryer to 400 pounds per hour @ 8% moisture, or almost twice the capacity without the use of deflocculants.

After the slip optimization, approximately 1,200 lbs of dry mix was prepared during this stage of the project. The mix was shipped to the TCNA facility in Anderson, SC for pressing and firing.

Tiles were dry-pressed at the Welco hydraulic press. Nominal tile size was 300x300 mm (12”x12”), at the thickness of 8.7 mm ($^{11}/_{32}$”). The bulk of the powder had moisture of 8%, and a portion of it was also tested at the 7% and 10% moisture which showed no visible difference in pressing and drying.

Green tiles were dried overnight at 105°C and fired in the roller kiln in two consecutive cycles, to simulate a longer commercial type kiln. The first (“bisque”) cycle, 81 minutes long, was to oxidize carbon in the raw mix and to provide initial consolidation of the kiln body at the temperature of about 800°C. The second cycle, 96 minutes long, was to accomplish the firing process at the final temperature of 1180-1190°C, as established by the preliminary test work at M.E. Tile Co.

Superimposing the bisque and firing cycles, we produced a hypothetical temperature profile of the proposed roller kiln of sufficient length. This profile is shown graphically on Fig. 1.

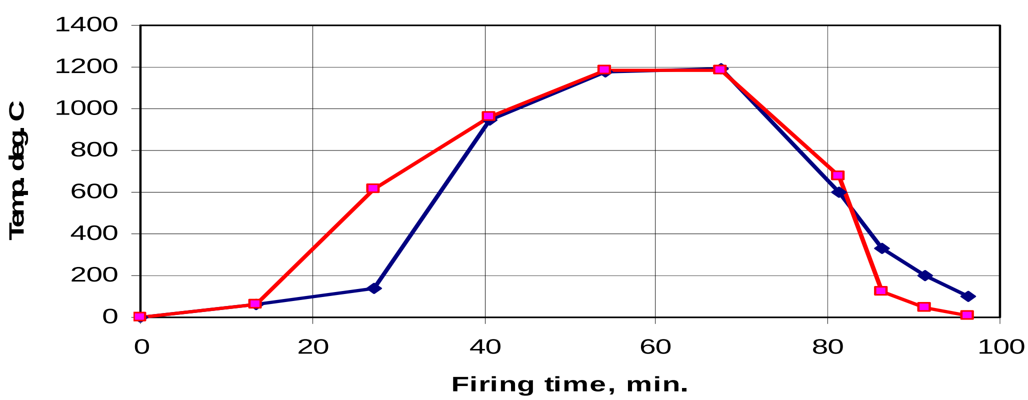

Fig. 1. Proposed extended temperature profile (upper and lower temperatures)

Testing of the tiles produced during this run showed significant improvement of the tile quality compared to all previous stages of work. In particular, water absorption was reduced. Breaking strength also improved (to 200 lbs) but still was below the standard requirements. This issue may be addressed in the further development, primarily by optimization of pressing and firing.

The next logical step is commercialization of the results of the project by establishing a demonstration production facility which will be able to produce tiles continuously, while possessing sufficient flexibility for fine adjustment of the process and developing potential for new applications. Such facility can be based on the existing TCNA test center, with addition of some drying, glazing, and material handling equipment. A budget estimate for such upgrade was obtained from a major Italian equipment manufacturer.

OBJECTIVES

The overall objective of this project is utilization of fly ash generated by burning of Illinois coal as the major raw ingredient for manufacturing ceramic tiles for wall, floor, and outdoor applications. This project was funded by the Illinois Department of Commerce and Economic Opportunity (DCEO) through the Office of Coal Development (OCD) and the Illinois Clean Coal Institute (ICCI).

In the previous phases of this program (Mishulovich, 2002 and 2004) a method was developed to overcome the detrimental 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 current phase of the project was to conclude the experimental work with a demonstration run using the typical equipment simulating the future commercial pressing and firing processes.

The technical goal of the current project was finalizing parameters of the technology for implementation at the commercial tile manufacturing plants. These parameters included physical characteristics related to wet mix preparation. 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 was needed to evaluate the behavior of ash-containing slips in the powder-preparation equipment. In particular, this work would assess rheological behavior of ash-based suspensions, determine the water demand of the slip, and proportioning of water-reducing admixtures. Bench top research of slip properties had to be conducted at CTL and M.E. Tile Co. Operation parameters of the spray dryer were to be investigated at the facilities of American Restoration Co. in Little Rock, AR, followed by pressing and firing at TCNA in Anderson, SC.

Another direction of the study had an objective of expanding the potential raw resources and bringing the tile quality up to the requirements for floor tiles that constitute a substantially larger market segment than wall tiles. This task included two sub-tasks. First, pre-oxidation of fly ash was to be tested as a way to utilize ashes with higher carbon content. Secondly, by further adjustment of the mix compositions, particularly, the flux proportion, we intended to improve the tile body density (characterized by water absorption) and to increase its breaking strength, in order to meet requirements for floor tiles. This task was done in cooperation with and at the facilities of M.E. Tile Co. The batch equipment of this plant provided the flexibility necessary for experimentation. Thereafter, the results were to be used in the tests at the pilot facilities.

INTRODUCTION AND BACKGROUND

Technical approach. 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 wasted. Therefore, any non-concrete utilization of the fly ash currently disposed in landfills would benefit the Illinois coal industry by removing serious obstacles to its use in the power industry. This project offers a technology which is not only environmentally sound and cost effective, but will also create a stable year-round demand.

As indicated above, the ultimate objective of the project was utilization of fly ash as the major raw ingredient for manufacturing value-added product, namely, ceramic tiles. Currently the domestic tile market is 313 million sq. meters. In the last 30 years it grew by a factor of 10. However, only a fraction of the market is now covered by the U.S. manufacturers, despite its significant overcapacity. The rest of the tiles consumed in the U.S. are imported, and the share of imports has been steadily rising during the same period from only 26% in 1975 to nearly 80% in 2005. One of the reasons why the U.S. manufacturers are less competitive is their high production cost. The average price of the U.S.-made tiles is almost twice the price of many imported tiles. The high cost of raw materials is an important contributing factor of such disadvantage. Utilization of fly ash that is being currently landfilled will reduce the raw materials cost and will provide a competitive edge to the U.S. manufacturers.

Considering the size of the tile manufacturing industry, a considerable fraction of fly ash produced in Illinois can be utilized to produce 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.

For the users and, consequently, producers of Illinois coal, the economic benefits associated with the manufacturing of ceramic tiles using fly ash are many: reduction in disposal costs, environmental benefits as fewer landfills need to be built, steady demand of fly ash throughout the year, and generation of additional revenue through marketing this value-added product. Such utilization is environmentally attractive, and the state economy will benefit from such an undertaking.

In the previous phases of this project a number of mixes of fly ash with clay and other conventional raw materials were tested in experimental tile manufacture. It was advantageous to maximize the fly ash proportion in the tile mixes, while retaining the product characteristics that are similar to those of commercially available tiles. Other mix ingredients are necessary to control processing parameters, such as firing temperature, shrinkage, surface texture, thermal expansion, etc.

Residual carbon in fly ash was identified as the principal source of the tile warping and bloating during firing. A processing method was developed to minimize the effect of compositional variability of fly ash on the product quality. The salient feature of this method was the specific firing temperature profile which provided for almost complete carbon removal by oxidation before sintering made the tile body impermeable. In addition, it was shown that to achieve physical characteristics comparable with those of commercial tiles, fly ash tiles required 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. 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.

The ceramic tile industry will accept this technology only after the technical and practical feasibility is demonstrated, and the parameters associated with commercial manufacturing are evaluated. The previous phases of the investigation focused on the proof of the concept and included laboratory-scale investigation, scale-up experimental work in a commercial tile manufacturing facility, and addressing the processing parameters and tile characteristics to develop data necessary for commercialization of this technology. The latest phase of the project (2004-2006) was directed on implementation of this technology at a pilot facility with typical equipment used to manufacture commercial tiles.

For the acceptance of this technology by the ceramic tile industry, it was deemed necessary to incorporate the commonly used wet preparation process into the test program. Also, it was desirable to bring the tile quality up to the more demanding floor tile specifications. This required additional experimental work on the bench- and pilot-scale scales.

Basics of tile manufacturing. Commercially, tiles are manufactured using three processing methods, namely, dry pressing, wet pressing, and slip casting. The properties of commercial tiles are controlled through the American National Standard Specifications for Ceramic Tiles (ANSI 137.1), published by the Tile Council of America (TCNA).

According to ANSI A137.1, tiles (glazed or unglazed), depending upon application, need to meet three acceptance categories: facial and structural defects, dimensional characteristics, and destructive tests. Of these three categories, destructive testing is directly associated with the properties of tile materials. Two most important numerical requirements are water absorption and breaking strength. Table 1 summarizes the physical characteristics of various types of tiles as specified by ANSI A137.1.

Table 1. Standard physical characteristics of ceramic tiles.

		Water absorption, %	Breaking strength, lbs
Unglazed	Mosaic tile	0.5 (porcelain)	250
	Quarry tile	5.0	250
	Paver tile	0.5 (porcelain)	250
Glazed	Wall tile	20.0	90
	Mosaic tile	0.5 (porcelain)	250
	Quarry tile	5.0	250
	Paver tile	0.5 (porcelain)	250

Dry pressing is the key process used now in large scale tile manufacturing. In this process, moisture of the clay mix is approximately 5 to 8% by weight. The mix is prepared almost exclusively by ***wet blending*** followed by ***spray drying***. This relatively dry powder is then pressed between metallic platens to form the green tile body. The floor and wall tiles produced by this method generally have a flat surface, and are called field tile. The production rate for this method may be very high. The formed “green” body is then fired and glazed.

Sintering forms solid bonds between particles when they are heated to appropriate temperatures. Such bonding reduces the surface energy by reducing the free surface. In this process, the grain boundaries are partially dissolved through grain growth, and the pore volume is reduced, leading to a compact mass. The temperature necessary to induce such bonding depends upon the characteristics of the material and the particle size distribution.

The firing conditions are critical in obtaining a densely sintered tile body. While the presence of unburned carbon in fly ash may add fuel value, it may also cause bloating. In order to avoid bloating, either the carbon in the green tile body has to be burned out by adjusting the firing schedule or burned out prior to mixing with the other raw ingredients for a fast firing high volume production line.

Glazing is performed by re-firing the sintered tile bodies at lower temperatures. Glazing improves the surface durability and adds different aesthetic values to tiles. While wall tiles are almost always glazed, floor tiles are not always glazed (ANSI 137.1).

Glaze is a glassy material designed to melt on the surface of a ceramic body and to stay adhered upon cooling. It is important that the thermal expansion of the glaze must be equal or slightly less than that of the ceramic body to avoid crazing.

Often an opaque coating called ***engobe*** is applied to the tile surface under glaze. Engobes are liquid clay slips of varying compositions used to give color to a piece, to improve the surface texture, to add textures, etc. Application of engobe enables tile manufacturers to maintain color consistency of glazed surfaces. This is often necessary for surface colors different from the natural color of the tile.

EXPERIMENTAL PROCEDURES

The experimental methods applied in this stage of the project tended to simulate the commercial production processes at pilot and small-commercial scales. Laboratory methods were used for analysis of raw materials and standard testing of products. Within this and the previous sub-tasks, tile water absorption was chosen as the main criterion of the tile quality.

Pre-oxidizing. One of the tasks of this program was development of the method that would remove carbon completely or partially by oxidizing fly ash prior to making tile mixes. Although the whole body of the previous work confirmed that carbon could be safely removed by a specially designed firing temperature profile, pre-oxidation would extend the resource base of the technology into the area of exceedingly high-carbon ashes.

With this objective, the following procedure was applied. Two batches of new fly ash and two batches of the ash used in the previous tests, about 11 lbs each, were placed in stainless steel trays in layers approximately 2 inch thick. Trays were heated in an electric furnace at 110°C/hour and held at 700°C for 90 minutes.

After cooling, the material was sampled at the top and bottom of each tray and analyzed for carbon content by TGA. In the latter test, the samples were heated in nitrogen to 700° to remove volatile matter not associated with carbon, and then heated isothermally in oxygen to oxidize carbon. This procedure was used to ascertain that the measured weight loss represented only fixed carbon, not total loss on ignition.

Mix proportion adjustments. The objective of this sub-task was to investigate the possibility of increasing the tile body density without a significant increase in the firing temperature. This goal was pursued by varying the content of fluxes in the mix.

In order to evaluate effects of increased flux content (talc, nepheline-syenite, frit) on tile characteristics, four mixes were prepared, using clays KT-1 (used also in previous work) and KT-556 (38%, dry basis). Pre-oxidized Vermillion fly ash was added (43%). Water was added in the amount of 19%, and additional 10% was added after the 7-day curing period. The balance consisted of wollastonite, talk, nepheline-syenite, and bentonite. The mix composition is shown in the following Table 2.

Table 2. Trial mix proportions, %

Mix components	4-05	5-05	6-05	7-05
Fly ash as is	43			
Fly ash calcined		43	38	38
Clay KTI-4	38	38	38	38
Wollastonite	4	4	4	4
Talc	3	3	4	3
Nepheline-	12	12	16	12
Bentonite	2	2	2	2
Frit				5

Powder preparation (pilot scale). In the previous pilot tests, the mix ingredients were pre-mixed and moistened to the required level immediately prior to pressing. This year's program was upgraded to include the powder preparation by the method emulating the commercial process. This sub-task was accomplished at the facilities of American Restoration Tile Co. (ART) in Little Rock, AR. The mix ingredients (see Table 3) were mixed with water on site and the resulting suspension (slip) dried in a relatively small commercial spray dryer.

Table 3. 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 ART facility has the essential units of the mix preparation equipment, namely a blending tank and a spray dryer. Following are technical characteristics of the dryer (see Fig. 2).

Type:	single nozzle, atomizer type dryer
Model:	1C-SC/100/UP
Manufacturer:	ICF-Industrie Cibec S.P.A., Maranello, Italy
Evaporative capacity	120 liters/hour
Thermal energy draw	100,000 kcal/hr
Fuel	natural gas
Spin chamber spiral:	4.0 mm thick
Nozzle size:	variable (1.0 mm used)
Pump pressure:	25-30 bar

Fig. 2. ICF-Industrie spray dryer

Pressing and firing (pilot scale). Tests at the research facility of the Tile Council of North America (TCNA), Anderson, South Carolina, were conducted on February 27 through March 2, 2005. The dry powder in the amount of about 1,200 lbs was prepared at ART and shipped to TCNA. The mix proportions are given in Table 3.

The TCNA 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 a maximum load of 650 tonnes (Fig. 3).

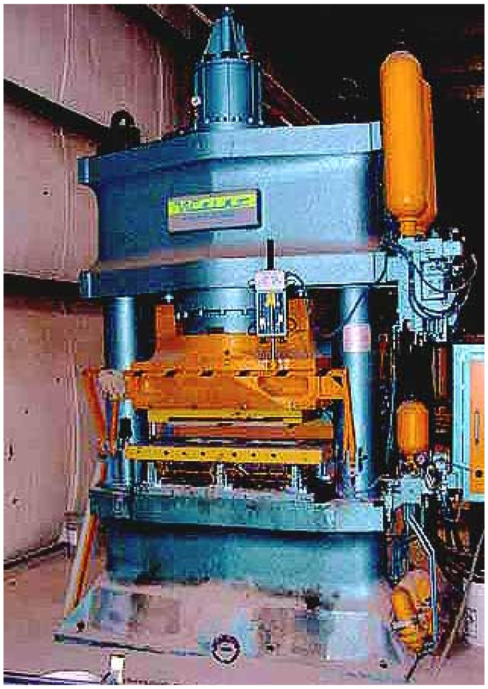

Fig. 3. WELCO hydraulic press

Pressed tiles were placed on racks (Fig. 4) and dried in an oven at 105°C for 3 hours prior to firing in a roller kiln.

Fig. 4. Green tiles loaded for drying

The kiln by Studio Uno (Italy) is a shortened version of a commercial kiln (Figs. 5 and 6). It consists of 9 sections, each 2 meters long (total length 18 m, or 60 ft).

Fig 5. Firing zone of the kiln (gas burners below and above rollers)

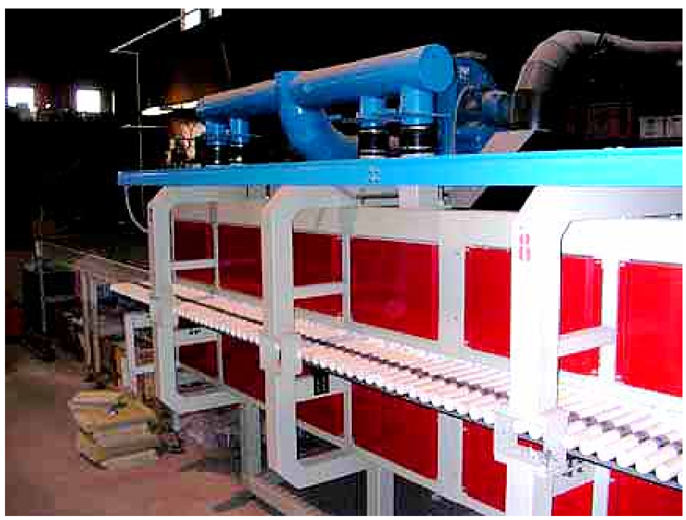

Fig. 6. Cooling zone of the kiln (cooling air tubes in white, flue gas in blue)

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.

RESULTS AND DISCUSSION

The following program tasks were often executed concurrently, and their timetables sometimes overlapped. The test results are described below according to the sequence presented in the original proposal.

Task 1: Mix Preparation and Tile Production under the Commercial Plant Conditions.

Slip preparation and adjustment. The essential part of the investigation of wet mix preparation was evaluation of the slip properties. It was established early in the experimental work that ash-based slip requires much higher water content than clay slip of the same viscosity. In the original tests with the ash-clay mixtures, to achieve the acceptable flow, the required water addition was 108% (on the dry basis). Drying such slip in the spray dryer would greatly reduce its production rate and energy efficiency. This necessitated testing of several water-reducing agents to achieve sufficient flowability at lower slip moisture.

With this objective, a series of tests was conducted at M.E. Tile Co. covering 28 sets of material with 8 variations of composition in each set. Fly ash was used in 3 forms:

- Virgin fly ash.
- Washed & dried fly ash.
- Washed, demagnetized and dried fly ash.

The following deflocculants and electrolytes were added to the slip in varying amounts:

- Barium carbonate.
- Soda ash.
- Sodium polyacrylate.

A usable slip using a combination of the above agents reduced the water addition to 51% (dry basis). The best results were achieved when the admixtures were added in the following proportions:

0.65% sodium polyacrylate

0.05% barium carbonate

0.65% soda ash

A small batch of tiles was produced from slip of this composition by casting in gypsum molds. Tiles were dried and fired at three levels of temperature. No visible signs of residual carbon were observed. Water absorption of the tiles is given in Table 4.

Table 4. Water absorption of slip-cast tiles.

Temp.°C		Water absorption,%.
1167	1	9.4
1167	2	7.9
1167	3	8.5
1167	4	7.6
1167	5	7.5
	Ave	**8.2**
1183	1	4.5
1183	2	4.2
1183	3	4.2
1183	4	4.0
1183	5	4.3
	Ave	**4.2**
1225	1	0.3
1225	2	0.3
1225	3	0.2
1225	4	0.3
	Ave	**0.3**

Prior to the deflocculant testing, the trial runs were conducted with slip containing 52% water (108% on dry basis) with addition of 0.50% of sodium polyacrylate. Optimization of the slip flow properties allowed for a drastic improvement of the spray dryer performance. The described combination of deflocculants was used to reduce the slip moisture. Table 5 compares the dryer performance before and after the slip optimization.

Table 5. Performance characteristics of the spray dryer

Parameter	Unit	Before	After
Slip moisture (dry basis)	%	108	50
Inlet temperature:	°C	520	410
Outlet temperature	°C	100 - 110	90-95
Pump pressure	bar	25-30	25-30
Body output @ 8% moisture	lbs/hr	210	400

Several batches of powder were produced with moisture ranging from 6 to 10%. Typical stereo photomicrograph of powder is shown on Fig. 7.

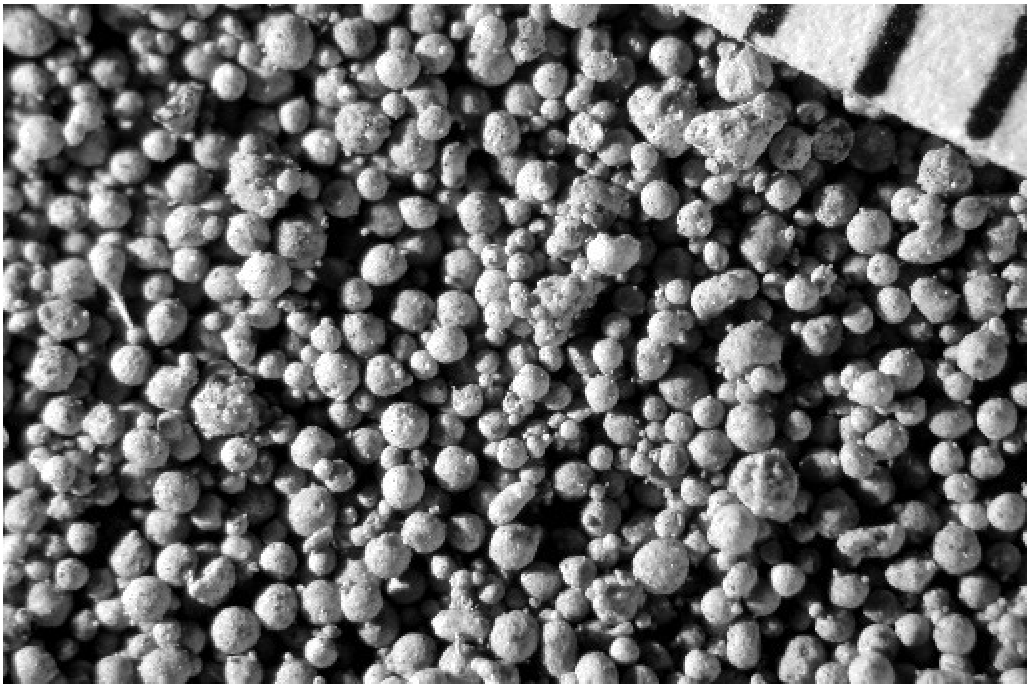

Fig. 7. Stereo photomicrograph of powder from the spray dryer

(1 scale division, top right = 1 mm)

Trial tiles from powders of varying moisture were pressed at the ART facility and fired at M.E.Tile Co. at two temperature levels. The tiles were subjected to the water absorption tests at CTL. The results are given in Table 6.

Table 6. Water absorption of dry-pressed tiles

Temp. ºC	Moisture,%	Water absorption,%
1159	6	9.0
1159	6	8.2
1159	6	8.3
	Ave.	**8.5**
1159	7	9.2
1159	7	9.4
1159	7	10.0
	Ave.	**9.5**
1159	8	7.5
1159	8	7.7
1159	8	7.9
	Ave.	**7.7**
1159	10	8.1
1159	10	8.1
1159	10	8.3
	Ave.	**8.1**
1183	6	3.9
1183	6	4.1
1183	6	4.7
	Ave.	**4.2**
1183	7	3.5
1183	7	3.6
1183	7	3.0
	Ave.	**3.4**
1183	8	4.2
1183	8	4.9
1183	8	4.3
	Ave.	**4.5**
1183	10	5.1
1183	10	4.7
1183	10	4.7
	Ave.	**4.8**

Comparing water absorption of slip-cast (Table 4) and dry-pressed tiles (Table 5), it can be concluded that the firing temperature of 1183°C (Cone 5) is sufficient for producing tiles with adequate density regardless of the production method. It may be also noted that the powder moisture of 7 – 8% gives better results that both higher and lower moistures.

Pilot scale pressing and firing. After the proper operation of the spray dryer was ascertained, powder was produced and shipped to the TCNA facility in Anderson, SC.

Tiles were dry-pressed at the Welco hydraulic press. Following are the principal parameters of pressing:

- Nominal tile size: 300x300 mm (12”x12”)
- Thickness: 8.7 mm ($^{11}/_{32}$”)
- Pressure: 120 to 160 kg/cm^2
- The bulk of the powder had moisture of 8%, and a relatively small portion of it was also tested at the 7% and 10% moisture which showed no visible difference in pressing and drying.

Green tiles were dried overnight at 105°C and fired in the roller kiln. The previous testing (2004) showed that the kiln was insufficiently long for simulating the commercial kiln temperature profile. This necessitated substitution of firing cycles for a conventional one-step kiln run. The first (“bisque”) cycle was to oxidize carbon in the raw mix and to provide initial consolidation of the kiln body. The second cycle was to complete the firing process.

Table 7 shows the firing schedules of both consecutive cycles. “Upper” and “lower” temperatures refer to the readings of thermocouples positioned above and below rollers.

Table 7. Firing schedule, roller kiln tests

Cycle, min	Upper temperatures	Lower temperatures
Bisque cycle		
9.7	50	50
9.7	106	372
9.8	624	651
9.8	686	619
9.8	786	798
9.8	601	657
8.7	286	80
8.7	200	50
5.4	100	10
Total time, min.		81.4
Firing cycle		
13.5	60	60
13.5	137	615
13.5	946	964
13.5	1176	1181
13.5	1189	1187
13.5	601	676
5.1	327	120
5.1	200	50
5.1	100	10
Total time, min		96.4

Total of about 240 tiles were fired under these schedules. Tiles were selected for testing to represent four quarters of the whole firing period (five samples per quarter). The average test results produced by the TCNA laboratory are given in Table 8.

Table 8. Characteristics of tiles (TCNA test)

	Breaking strength, lbs	Water absorption, %
First quarter	191	8.4
Second quarter	190	7.7
Third quarter	203	8.0
Fourth quarter	211	7.4

These results show measurable improvement over the previous pilot-scale tests. Both strength and water absorption approached although not quite reached the standard requirements. The most immediate ways to further improve the tile quality are optimization of the pressing regimen and increase of the tile density by addition of fluxes and/or slight increase of the firing temperature. The latter, as well as the press optimization, could not have been accomplished without some modifications to the subcontractor's (TCNA) equipment.

In the mean time, based on the schedules Table 7, a combined temperature profile was designed for a hypothetical extended kiln which would incorporate both bisque and firing cycles (Table 9).

Table 9. Proposed extended firing schedule

Cycle, min.	Upper temperatures	Lower temperatures
9.7	50	50
9.7	106	372
9.8	624	651
9.8	686	619
13.5	946	964
13.5	1176	1181
13.5	1189	1187
13.5	601	676
5.1	327	120
5.1	200	50
5.1	100	10
Total time, min.		108.4

This schedule is shown graphically on Fig. 1 (Executive Summary).

Task 2: Mix Variations.

This part of the project, originally designated in our proposal as Task 2, was largely conducted concurrently with the test work described above and was completed prior to the pilot tests.

A new batch of fly ash was procured from the Dynegy Vermillion power plant. The material was analyzed at CTL by XRF (Table 10).

Table 10. Chemical composition of Vermillion fly ash

Analyte	Weight %
SiO_2	46.54
Al_2O_3	22.70
Fe_2O_3	15.01
CaO	5.80
MgO	0.80
SO_3	1.14
Na_2O	2.05
K_2O	2.05
TiO_2	1.16
P_2O_5	0.11
Mn_2O_3	0.10
SrO	0.03
Cr_2O_3	0.03
ZnO	0.04
L.O.I. (950° C)	1.96
Total	99.52

Carbon content was analyzed by TGA (Fig. 8).

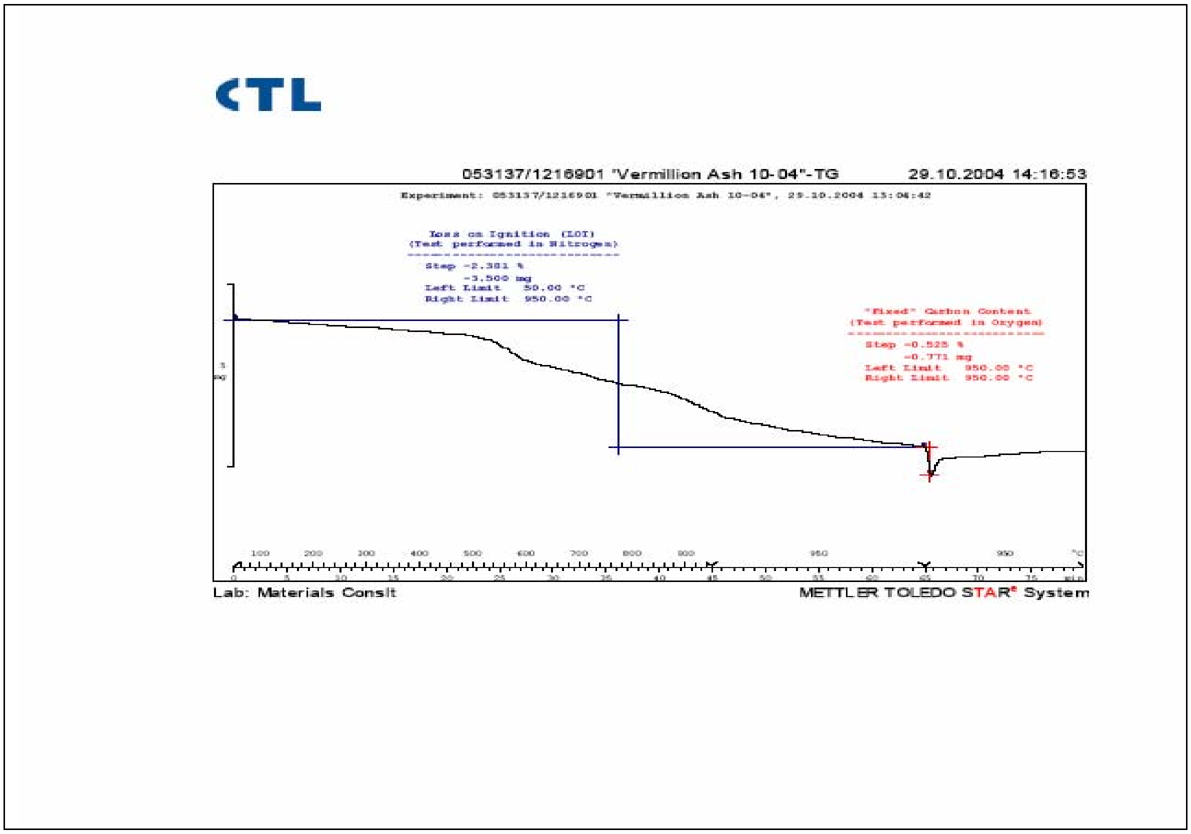

Fig. 8. Determination of fixed carbon in fly ash by TGA

Particle size distribution was analyzed by a laser diffractometer (Fig. 9).

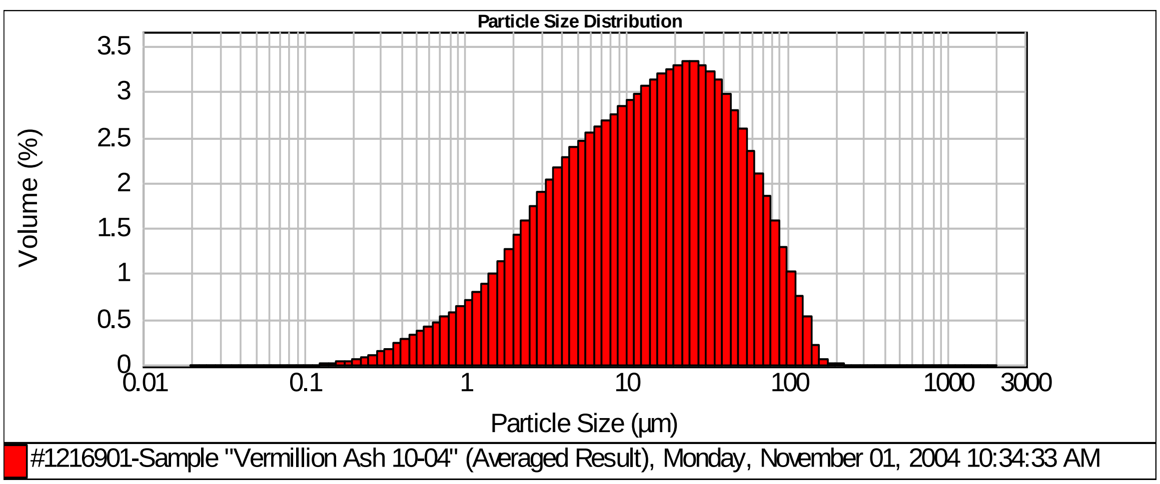

Fig. 9. Particle size distribution of Vermillion fly ash

Pre-oxidation. Besides carbon removal, additional benefits of pre-oxidation are (1) allowing firing at a higher temperature to increase strength of the tile, and (2) reduction of the voids in the fired tile body leading to a denser body texture.

The results (see Table 11) indicated that carbon removal by pre-oxidation may be accomplished at a sufficient rate by pre-oxidation.

Table 11. Residual carbon in ash samples

	Tray	New ash (2004)	Tray	Old ash (2002)
Original	-	0.53%	-	2.32%
Top ¼”	#1	0.01%	#3	0.02%
	#2	0.02%	#4	0.06%
Bottom ¼”	#1	0.02%	#3	0.02%
	#2	0.02%	#4	0.46%

Pre-oxidized ash was tested in mixes with clay KT-1 (38%, dry basis). The balance consisted of wollastonite, talk, nepheline-syenite, and bentonite. Tiles (58 total) were fired at variable temperatures, with and without one-hour hold at 700°. Density of the tile bodies was assessed by the water-absorption tests (Table 12). Previously it was demonstrated that water absorption is closely correlated with the breaking strength. The test of this series of tiles showed that, using mixes with pre-oxidized ash at firing temperatures over 1180°C, hold is not necessary since it does not further reduce the tile water absorption.

Table 12. Average water absorption of tiles

Temp. °C	Hold @700	Abs. %	Temp. C	Hold @700	Abs. %
1159	0	4.5	1159	60	3.7
1183	0	0.3	1196	60	0.4
1213	0	0.5	1213	60	0.4
1234	0	0.7	1234	60	0.6

The results of this study have demonstrated that the problem of the residual carbon could be resolved by two different or complementary methods. Carefully designed temperature profile can produce sound tile bodies from mixes with moderate amount of carbon. With higher carbon content pre-oxidation may prove more efficient thus expanding the field of usable ash sources. In our tests the high proportions of fly ash (up to 50%) were used without any detrimental effects in commercial manufacturing of ceramic tiles.

Mix proportion adjustments. The objective of this sub-task was to investigate the possibility of increasing the tile body density without a significant increase in the firing temperature. This goal was pursued by varying the content of fluxes in the mix. Besides nepheline-syenite, talc, etc. frit was added in one of the mixes to obtain the desired characteristics (see Table 2).

Total of 76 tiles were prepared from these mixes by plastic forming in a roller press. After drying, tiles were fired in the electric kiln at 1149°C, 1161°C, and 1185°C and tested in the CTL laboratory for water absorption. Summary of the tests is given in Table 13.

Table 13. Average water absorption of tiles, %

Mix ID	Mix characteristic	1149°C	1161°C	1185°C
4-05	Basic, ash as received	9.0	6.9	1.7
5-05	Basic, ash calcined	7.0	4.0	0.3
6-05	Ash calcined, nepheline-syenite added	6.7	3.6	0.3
7-05	Ash calcined, frit added	2.8	0.5	0.6

Future developments. The next logical step is commercialization of the results of the project by establishing a demonstration production facility which will be able to produce tiles continuously, while possessing sufficient flexibility for fine adjustment of the process and developing potential for new applications. Such facility can be based on the existing TCNA test center, with addition of some drying, glazing, and material handling equipment. A budget estimate for such upgrade was obtained from a major Italian equipment manufacturer (see Appendix).

CONCLUSIONS AND RECOMMENDATIONS

- The key findings of this project confirmed that ceramic tiles for floor and wall application can be produced from mixes containing up to 43% of fly ash with moderate content of residual carbon.

- Studies at the laboratory and small-production scales demonstrated that residual carbon could be removed by two principal methods, (1) by oxidation of the formed tile bodies in kilns with carefully selected firing schedule, or (2) by oxidation of fly ash prior to mix preparation.

- Material composition of raw mixes largely determines physical characteristics of tiles and parameters of the manufacturing process, both in mix preparation and in firing. Experimental work wherein the mix proportions and admixtures varied resulted in the development of optimized mixes suitable for pilot production.

- Rheological characteristics of fly ash slips made in the process of the mix preparation are different from those of conventional clay slips in terms of higher viscosity and much higher water demand. A combination of chemical agents (deflocculants) was shown to be required to produce pourable slips at moderate moisture.

- Experimental runs using commercial-type production equipment, including drying, pressing, and firing in a roller kiln, demonstrated that tiles meeting the standard water absorption requirements can be produced from mixes with over 40% of fly ash with substantial carbon content. Increase of the tile breaking strength may require further optimization of the pressing regimen.

- 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. As a first step towards large-scale production would be a small continuously operating production line that can be built based on the existing TCNA facility.

REFERENCES

Mishulovich, A., J.L. Evanko, 2002. UTILIZATION OF ILLINOIS FLY ASH IN MANUFACTURING OF CERAMIC TILES. Technical Report No. 00-1/3.1B-6. Construction Technology Laboratories, Skokie, Illinois.

Mishulovich, A., J.L. Evanko, 2004 UTILIZATION OF ILLINOIS FLY ASH IN MANUFACTURING OF CERAMIC TILES. Technical Report No. 02-1/3.1A-82004, Construction Technology Laboratories, Skokie, Illinois.

DISCLAIMER STATEMENT

APPENDIX

LIST OF EQUIPMENT

(as submitted by ***Studio 1 Automazioni Industriali***, Italy – prices in euros)

1.	PRESS UNLOADING SYSTEM, including press take-off table, overturning unit, roller way with lifting belts for row evacuation, electric material board, electric plant	22.720,00
2.	DRYER LOADING ROLLER WAY	16.800,00
3.	SINGLE LAYER ROLLER DRYER, total length 6,6 m	55.000,00
4.	DRYER UNLOADING ROLLER WAY	17.450,00
5.	GLAZING LINE , COMPLETE WITH DRIVE GROUPS , ELECTRIC PLANT, DOUBLE DISC CABIN, WATER SPRAY BOOTH, SPRAY GUN, BRUSH FAN	65.000,00
6.	LINE UNLOADING ROBOT	32.275,00
7.	KILN LOADING ROBOT	32.275,00
8.	TRANSPORT LINE , for kiln loading	7.100,00
9.	KILN LOADING ROLLER WAY	16.800,00
10.	STORAGE CARS complete with 375 trays	14.700,00
11.	PRE-HEATING SECTIONS (including electrical)	56.250,00

TOTAL AMOUNT €336.370,00 ($ 410,371.40)

Proposed layout of the TCNA research facility with added equipment