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Ceramic Tiles from High-Carbon Fly Ash

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ABSTRACT
Only about 20% of Illinois fly ash is utilized, mostly by the concrete industry. Use of fly ash as a major ingredient in manufacturing ceramic tiles can increase the ash utilization, as well as reduce the cost of raw materials in the tile industry and provide a competitive edge to U.S. tile manufacturers against foreign competition.

The project included laboratory characterization of the materials, scale-up investigation in a custom tile manufacturing facility, and trials with large-scale industrial equipment.

A process was developed that allows utilization of fly ash with moderately high carbon content in manufacturing ceramic tiles. The method leads to oxidizing the residual carbon, thus removing a potential source of tile warping, surface defects, and loss of strength. The approach was based on holding the tiles at the temperature sufficient for carbon oxidation, before the liquid phase formation seals the system of pores supplying oxygen to the tile's interior. Subsequently, tiles were heated to the firing temperature when sintering and fusion combined to form a tile body with low porosity and adequate strength.

The pilot-scale experiments and successful runs on the actual mass-production, industrial-type equipment indicated that characteristics of fly ash-based tile bodies are superior to those required for wall tile applications, and comparable to those required for floor and outdoor applications. The developed processing method has general applicability to other Class F fly ashes as well. It has also been confirmed that fly ash tiles with low water absorption can be made at temperatures significantly lower than those required for conventional ceramic tiles.

Introduction. Annually, the state of Illinois produces over 5% of the 60 million tons of fly ash generated in the U.S. Only about 20% of this fly ash is utilized by the cement and concrete industry, and the majority of the rest is landfilled. Any non-concrete utilization of the fly ash currently being disposed will not only be environmentally sound and cost effective, but also will create a stable year-round demand.

The overall objective of this project was to utilize fly ash generated by burning of Illinois coal as the major raw ingredient for manufacturing ceramic tiles for wall, floor, and outdoor applications. 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 contribute to the major cost in running a tile plant, replacement of costly raw materials by fly ash is attractive to tile manufacturers. Such utilization is environmentally attractive, and the state economy will benefit from such an undertaking.

Tile manufacturing process. The predominant raw material for ceramic tiles is clay. Various processed clays are available for the industry and offer a range of thermal characteristics, plasticity, color, and fineness. Actual mixes for tile manufacturing contain one or several types of clay and additions, such as fluxes (talc, nepheline syenite, wollastonite.)

Preparing mixes of clays and other ingredients at the production facility can be done by different ways, which in turn determines the subsequent processing methods [Jones and Berard, 1972]. Three methods are presently used: dry pressing, wet pressing, and slip casting.

- In dry pressing, the raw mix contains about 5% of water (based upon the weight of solid). The floor, wall, and outdoor tiles produced by this method mostly have a flat surface, and the production rate for this method may be very high.

- In wet pressing, the amount of water used is higher (approximately 25%), and the resulting material has the consistency of putty. This process has the advantage of reasonably high production rates, and fairly complicated designs are adequately reproduced.

- In the slip casting method, a self-supporting shape, called a cast, is produced in a water-absorbent mold from a specially formulated slip, i.e. semi-liquid mixture of clay and water. Any intricate designs can be adequately reproduced in this processing method. However, a number of parameters play an important role in successful slip casting, which is even more complex in the presence of the multimineralic material, such as fly ash.

All these processes produce so-called green tile body, which is then fired at approximately 1,100°C to produce sintered tiles. In *most* cases, the fired tile bodies are glazed in a secondary firing at a relatively lower temperature. Glazing improves the surface durability and adds different aesthetic values to tiles. A glaze is a glassy material designed to melt on the surface of a ceramic body, and to stay adhered upon cooling.

Properties of tiles. Acceptance criteria for commercially produced tiles may be subdivided into three categories: facial and structural soundness, dimensional characteristics, and physical properties. Of these categories, the latter is directly related to the properties of tile materials. Therefore, the tile bodies, regardless of their application, need to satisfy the two most important requirements, water absorption and breaking strength (reflecting tensile strength). The tile bodies are customarily classified by their water absorption as shown in Table 1.

Table 1. Classification of tile bodies

	Water absorption, %
Non-vitreous	>7.0
Semi-vitreous	3.0-7.0
Vitreous	0.5-3.0
Impervious	<0.5

Table 2 summarizes the physical characteristics of various types of tiles as specified by the existing standards.

Table 2. Standard physical characteristics of ceramic tiles

		Water absorption, % (max.)	Breaking strength, lbs (min.)
Unglazed	Mosaic tile	3.0	250
	Quarry tile	5.0	250
	Paver tile	5.0	250
Glazed	Wall tile	20.0	90
	Mosaic tile	3.0	250
	Quarry tile	5.0	250
	Paver tile	7.0	250

Fly ash as raw material. In 2001, about 100 ceramic tile-manufacturing plants in the United States produced 620 million square feet of tiles, and the quantity is expected to rise in the near future. This number, however, covered only 26% of the total U.S. demand, the balance being supplied by imports. Because of the high cost of raw materials, U.S. manufacturers are less competitive than their foreign counterparts.

Owing to its chemical composition and physical characteristics, fly ash can be used as partial replacement for clay in the ceramic tile industry. The composition of fly ash is such that it can be used as a major raw ingredient for making wall and floor tiles. The ash chemical composition is shown in Table 3 in comparison with a typical clay used in tile manufacture and a prospective clay/fly ash blend as an alternative raw material.

Table 3. Chemical Composition of Materials

	Ball clay	Fly ash	Blend
SiO_2	57.6	51.65	53.35
Al_2O_3	27.5	23.52	24.55
Fe_2O_3	1.1	9.39	4.46
CaO	0.2	4.73	4.04
MgO	0.4	1.07	1.64
Na_2O	1.5	1.73	3.13
K_2O	0.2	2.32	1.99

In fly ash, the rounded particles with a wide distribution in size are predominantly glassy. The glass content in fly ash is generally higher than 70% [Helmuth, 1987]. Vitreous (glassy) phase plays an important role in sintering [Kingery et al., 1976]. The angular particles are mostly comprised of crystalline solids, such as quartz, mullite, magnetite, and hematite. When the combined amount of the acidic oxides (silicon, aluminum, and iron) is 70% or above, it is described as a Class F ash. When this amount is between 50 and 70%, the ash is called a Class C ash. Power plants burning Illinois coal produce primarily Class F ash.

Particle size distribution of a typical ash is shown on Fig. 1.

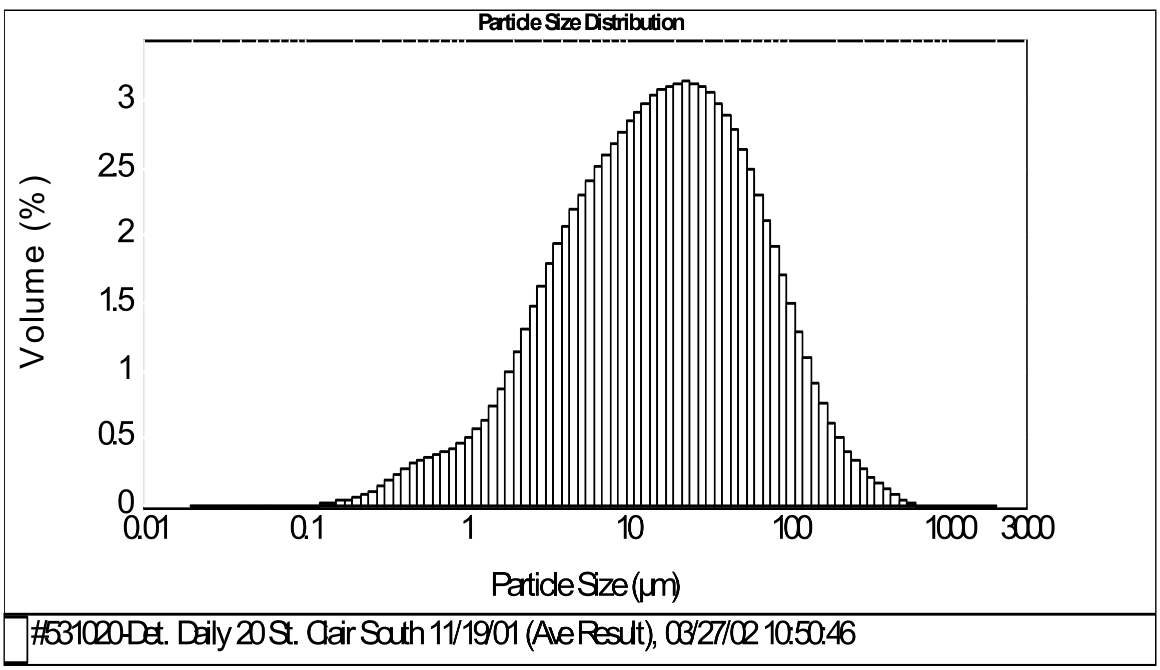

Fig. 1. Particle size distribution of fly ash

It is obvious that the fine powder habit of fly ashes makes them usable in the as-received form without any further size reduction.

Therefore, utilization of fly ash for making ceramic tiles is very attractive. Such utilization is environmentally sound, preserves our resources, creates a year-round demand for fly ash, and benefits the economy of the state.

Experimental. High carbon content is potentially the most important characteristic of fly ash that may have an adverse effect on the process implementation. Whereas carbon is easily burned out on the tile surface, its particles can be entrapped inside the tile body and cause a wide range of defects during sintering. In extreme cases it results in swelling and delamination. Blistering, or formation of swollen patches on the tile surface, or bloating of the entire tile body was an issue for the first firing tests conducted with ash-containing mixes. Thereafter the major part of this project focused at the development of practically feasible measures to remove the carbon particles from fly ash or to alleviate its effects.

First, the attempt was made to preheat fly ash in order to remove carbon and volatiles before blending with other mix ingredients. Fly ash was heated at 20°C per minute to 800, 900, 1000, 1100, and 1200°C. It was observed that above 800°C, fly ash started to sinter, and at 1000°C it formed a fairly hard mass. It was apparent that in a large-scale commercial production this approach was impractical. More realistic would be the one-step thermal treatment combining carbon removal by oxidation with sintering. The development of the temperature profiles of such process was the principal objective of trial tests in laboratory electric furnaces and in commercial-size batch furnaces at M.E. Tile Co.

To minimize or eliminate effects of carbon on the tile appearance, two approaches were conceived. The first was fast firing. It was based on severely limiting oxygen access to the carbon in the tile body interior. During firing, oxidation of the present carbon begins at a temperature below 700ºC. A few different untreated fly ashes with carbon content ranging from 3 to 20% were mixed with other ingredients and fired at a rate of as high as 40°C/minute to 1,200°C. When tiles were fired at this high speed of the temperature rise, the tile surface sintered and became virtually impervious to air. As a result, carbon particles encapsulated inside the specimen were not oxidized and did not generate any internal pressure to cause bloating. In this fast firing, most of the tile bodies showed no surface deformation. At the same time, the residual carbon did not seem to have any effect on the strength.

However, these results were not consistently positive. Evidently, variations of porosity and compactness of formed tile body could be a contributing factor to this phenomenon. Besides, the black core of carbon-rich material may be undesirable from the standpoint of the tile appearance.

A more satisfactory solution to this carbon problem was slow firing. At slow firing rate, carbon burns out while the piece being fired remains porous. First, several tile bodies were fired in a laboratory furnace using different firing schedules. Air has been passed through the furnace to intensify the oxidation and shorten the time needed to decrease the carbon content to an acceptable level. It was observed that holding the tile in the furnace at 750°C for 12 minutes is adequate for an approximately 10 mm thick tiles to burn the interior carbon particles (see Table 4).

Table 4. Tile Characteristics

Sample No.	Firing time, min.	Breaking load, lbs	Visible carbon
1	12	341	Abundant
2	15	346	Minimal
3	15	225	Minimal
4	18	295	None
5	18	318	None

After the key process parameters were studied at the laboratory scale, the experiments were transferred to the small commercial scale production facility at M.E. Tile Co. Green tiles were produced by wet ram pressing, roller pressing, and slip casting. The tiles were fired in electric kilns with programmable controllers.

A number of test firings under varied temperature profiles were conducted in order to minimize or eliminate dark core near the center of the fired tile bodies. Under the optimal conditions that have been established, tile bodies could have been prepared with virtually no dark core.

A number of process parameters *were* varied in order to develop the optimized mix composition and firing conditions. To determine the effect of moisture on the pore structure, the tiles were pressed and fired from the mixes with the different water content. Experimental firings were also conducted with mixes containing fluxes (nepheline-syenite, talc) to optimize the firing temperature and reduce water absorption. The results helped to finalize the mix composition intended for the pilot tests at the TCA facility.

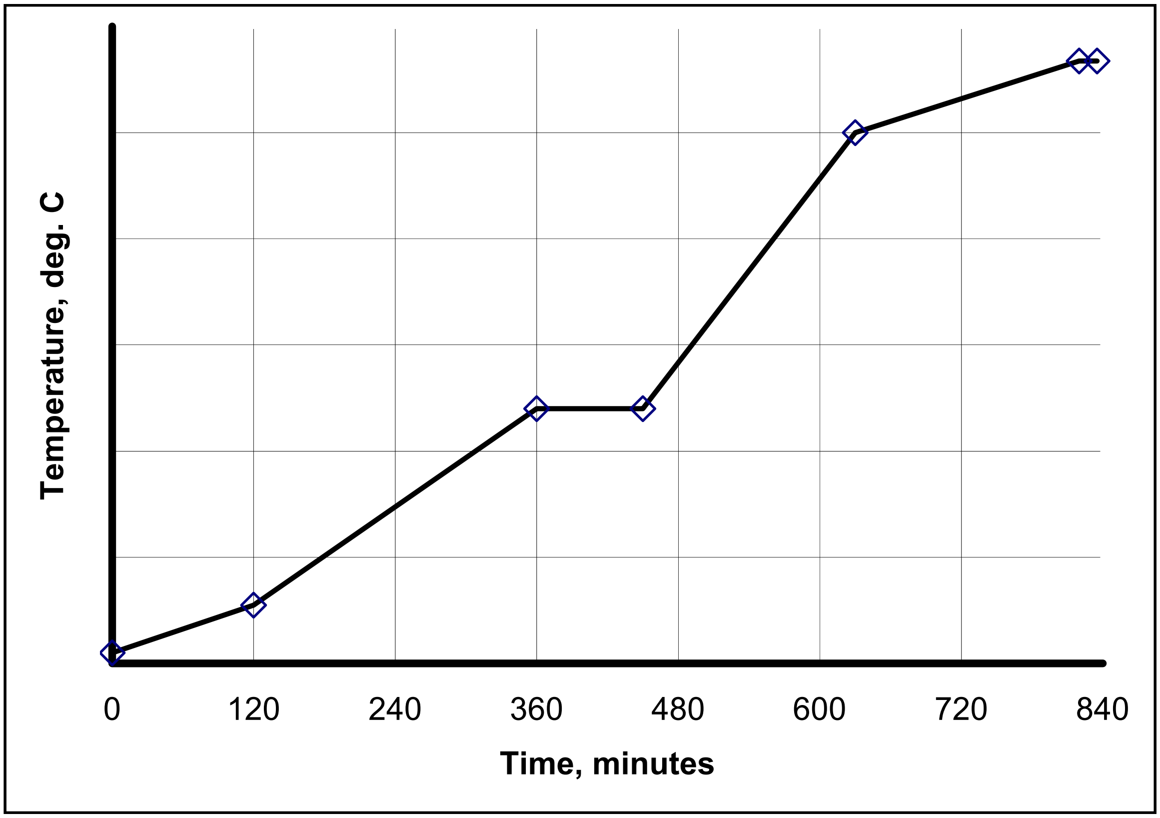

Fig. 2. Typical temperature profile

When tiles were produced without disqualifying surface and dimensional defects, they were subjected to physical testing. The tile bodies were tested for breaking strength by the test method ASTM C 648 based on a three-point support and a single point loading.

Water absorption is a reliable indicator of the degree of the tile body sintering. The following Table 5 gives an example of the results of water absorption tests for one of the mix compositions (average for batches of 8) as a function of the firing temperature.

Table 5. Water absorption of tiles

Sample No.	Firing temperature, ºC	Water absorption, %
1	1086	11.3
2	1117	11.1
3	1152	10.6
4	1175	7.7
5	1184	6.6

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While slight reduction in water absorption with progressive firing temperatures is obvious, a substantial decrease in water absorption occurred between 1152 and 1175°C, and continued to the final firing temperature of 1184°C. In further tests, improvements of the firing conditions led to producing tiles with water absorption as low as 0.3 to 0.5%.

Statistical analysis of the physical test results produced by testing several batches of tiles demonstrated very close correlation between firing shrinkage and porosity of the fired tiles (correlation coefficient $r = -0.92$). Correlation between shrinkage and breaking strength was statistically significant at the 99% level.

Pilot tile production. The project was brought to conclusion by the pilot production of tiles at the TCA research center in Anderson, SC. The facility has two pieces of the core tile-making equipment, namely a hydraulic press and a roller kiln. The press by WELKO (Italy) is a commercial model with maximum load of 650 ton. The kiln by Studio Uno (Italy) is a shortened version of a commercial kiln.

Because of the experimental nature of the test run, the press and the kiln were operated in a batch mode. The press was loaded manually. The green tiles were oven dried and loaded into the kiln. Individual tiles were pressed and fired under varying conditions in order to define the optimum conditions. Efficient carbon removal was the main criterion of the process optimization.

Process parameters were set in the course of testing as follows:

Tile size: 300x300 mm (12”x12”)
Thickness: 7.1 mm to 8.7 mm ($^{9}/_{32}$” to $^{11}/_{32}$”)
Moisture: 7 to 7.7%
Pressure: 190 to 220 kg/cm^{2h}
Firing time: 60 to 100 minutes
Pre-heating temperature: 660 to 740ºC
Firing temperature: 1143ºC
Pre-heating time: 24 to 50 min.

After the tiles were manufactured standard tests were performed to verify their compliance with the standard specifications. Average water absorption was 14.5%, and average breaking strength, 255 lbs.

Discussion. In the course of this study, the processing method was developed that allows utilization of Illinois coal fly ash with moderately high carbon content in manufacturing ceramic tiles. The results demonstrate that high dosages of fly ash can be used in successful commercial manufacturing of ceramic tiles using wet pressing, slip casting, and dry pressing methods. The cause of the problems relevant to processing and aesthetics have been identified, and remedial measures developed. The temperature profile of firing was developed that leads to oxidizing residual carbon from the ash and removal of a potential source of the tile warping, surface defects, and loss of strength. The characteristics of fly ash-based tiles are superior to those required for wall tile applications, and comparable to those required for floor and outdoor applications. Also, the processing method developed has general applicability to other Class F fly ashes, although some specific processing steps may need adjustments due to significant shifts in the fly ash characteristics.

The marketing and economic feasibility study based upon this concept confirmed that considering the size of the tile industry, a reasonable fraction of the fly ash produced in Illinois can be utilized to prepare ceramic tiles. Pursuing this technology is also important from the tile manufacturer's viewpoint, as raw materials contribute to a major cost of running a tile plant. Replacement of costly raw materials by less expensive fly ash would not only be attractive to tile manufacturers, but also it would make the U.S. tile industry more competitive against the foreign imports. It makes perfect sense to build a tile plant close to or at the property of a utility company. The latter can also add value to its waste material (fly ash) if its characteristics are stabilized at the specified level by homogenization.

The next step in the development of the proposed technology would be producing a batch of tiles in the continuous mode on the prototype equipment suggested for the prospective commercial plant. Such test would provide all information necessary for the actual plant design and engineering.

CONCLUSIONS

1. The results produced in this program confirm that fly ash-based tiles can be successfully made from mixes containing close to 40% of fly ash.
2. The temperature profile of thermal treatment was developed providing optimum conditions for carbon removal by oxidation.
3. The results obtained in the small batch commercial production were further confirmed by the experimental run on the mass production commercial equipment.
4. The marketing and cost analysis indicates that it would be economically feasible to construct a full-scale tile plant based on the technology developed in this project.

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