Improving Freezing and Thawing Properties of Fly Ash Bricks

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ABSTRACT

In 2004, the National Science Foundation (NSF) funded a Small Business Innovation Research (SBIR) Phase 1 grant to Freight Pipeline Company. The purpose of the grant is to improve the freeze/thaw properties of compacted fly ash bricks, so that such bricks will not deteriorate prematurely in cold climate, and they can be used anywhere in the United States for various commercial purposes.

It has been established through previous research that by mixing Class-C fly ash with approximately 10% water, strong fly ash brick can be produced at compaction pressure of 3,000 psi, approximately. The bricks produced, upon two weeks of curing, have compressive strength exceeding that required by ASTM for ordinary bricks. The fly ash bricks also have good water absorption property and low permeability. However, they can only survive about 8 cycles of freeze/thaw, which is far short of the ASTM-Standard requirement of 50 cycles. Once this freeze/thaw property of the flyash bricks is improved sufficiently to pass the 50-cycle ASTM Standard, the brick will have an excellent future for commercial acceptance.

With the NFS funding, Freight Pipeline Company tested various methods designed to improve the freeze/thaw property of the compacted fly ash bricks, including: (1) using higher compaction pressure and optimum fly-ash-to-water ratio, (2) adding a small amount of fiber to the fly ash before compaction, (3) adding some cement or lime to the fly ash before compaction, (4) using certain liquid sealants to coat the bricks, (5) using a higher compaction pressure to make stronger bricks, (6) lengthening the curing time in order to make stronger bricks, (7) use of a split mold to make better bricks, and (8) use of an air-entrainment agent to improve the freeze/thaw property of the bricks.

The tests showed that some of the methods that further improve the compressive strength of the brick do not necessarily result in an improvement in the freeze/thaw property. For instance, method 3 (adding 5% Portland cement or lime), method 1 (using higher compaction pressure), and method 6 (lengthening curing), all result in stronger compressive strength of the fly ash brick, but they have no beneficial effect on enhancing the freeze/thaw property of the fly ash brick. On the other hand, methods that do not enhance the compressive strength of the fly ash brick, such as using fiber (method 2) and air entrainment (method 8), did show significant improvement of the freeze/thaw property. With all practical matters taken into account, including freeze/thaw resistance and simplicity in processing, the air entrainment method appears to be the most effective and practical. It enables the bricks to pass the 50-cycle freeze/thaw without damage. More tests are currently underway to evaluate the effectiveness of air entrainment

method under various conditions, and to determine the optimum amount of the air-entrainment additive needed to enhance the freeze/thaw property of the fly ash brick.

1. INTRODUCTION

Coal is the prime resource for generating electricity in the United States and in many other nations. Approximately 57% of the electrical power in the United States is generated from coal [1]. According to the U.S. Department of Energy [2], in 2003, the nation produced and used approximately 1.07 billion tons of coal. Due to environmental and health concerns, coal-fired power plants are required by law to remove the particulates contained in smoke before the smoke is allowed to be emitted through stacks or chimneys. The particulates removed from the smoke – fly ash-- is the most abundant coal combustion product (CCP) that exists at coal-fired power plants. For years, fly ash has been used as an additive to cement for making concrete for structural use, as a material for constructing embankment and the roadbed of highways, as an additive to stabilize soil, and in many other applications [3]. Still, the bulk of the fly ash generated in the nation is not used, ending up as a waste material causing waste disposal problems.

According to the American Coal Ash Association [3], power plants in the United States in 2003 produced approximately 120 million tons of coal combustion byproducts, of which about 70 million tons are fly ash. Only about 39% (27 million tons annually) of the fly ash in the nation is utilized, the rest (61% or 43 million tons annually) are disposed of either in specially designed landfills, slurry ponds, or mine pits. It constitutes a huge waste of a valuable resource, a significant cost to power plants, and a significant environmental problem – wasting land for disposal and creating potential pollution to surface and groundwater. There is a strong need by both electric utilities and the public to increase the utilization of fly ash.

This project is intended to provide a solution to the fly ash disposal problem by developing a new way to use fly ash – making brick and other construction block materials. Because currently the nation uses about 9 billion bricks a year [4], which is equivalent to about 20 million tons of bricks per year, using fly ash to make bricks constitutes a large potential market of fly ash, especially if the bricks are made of 100% fly ash. Using fly ash to make bricks not only solves a solid waste disposal problem but also helps the environment in other ways such as the following:

- Use of fly ash to make bricks and blocks reduces the use of concrete bricks and blocks, which are made of cement and aggregates. In manufacturing cement, a large amount of fossil fuel is burned to generate the high temperature needed to produce the cement. For each ton of cement produced, approximately a ton of carbon dioxide is generated, which contributes to global warming [5]. In contrast, the process used in this project to make fly ash bricks and blocks requires no heating and no combustion of fossil fuel. Thus, using this process to make bricks and blocks instead of using cement to make bricks reduces greenhouse gas and slows down global warming.
- Use of fly ash to make bricks also reduces the use of clay bricks. In making clay bricks, the green bricks must be heated to over 2000 ^{o}F (more than 1000 ^{o}C), which uses much energy provided by burning fossil fuel. Since the fly ash brick technology developed by this project does not require heating, again it helps to reduce greenhouse gas and global warming by using this process instead of using clay bricks.

The technology studied in this project utilizes the natural binder (i.e., the cementitious materials, mainly lime in the form of CaO) that exists in Class C fly ash to make bricks and blocks. The bricks are made by mixing Class C fly ash with a small amount of water to form a mixture, compacting the mixture in a mold at a pressure higher than 1000 psi (6.9 kPa), dislodging the green brick from the mold, and then curing the dislodged brick in a wet environment (curing chamber) for at least 2 weeks -- to allow the product to harden and gain strength. The entire process is done under room temperature, and is relatively simple and inexpensive.

Previous research found that when this type of fly ash bricks is mass produced, the production cost including a 15% return-on-investment (ROI) is estimated to be less than 7 cents per brick [6]. As compared to the wholesale price of $300 to $400 per thousand bricks of ordinary types (either clay brick or concrete brick), this type of fly ash brick is expected to cost much less than, and will have a cost advantage over, ordinary bricks. Furthermore, the brick is far more uniform in size and geometry than ordinary bricks (see Figure 1 below), which makes brick-laying easier (saves labor), in addition to saving mortar in brick joints. Since brick-laying is rather labor intensive, being able to save labor is highly important to contractors and builders. A 10% saving in labor can mean savings of close to 8 cents per brick for the contractor [7]. Thus, the uniformity of the compacted fly ash brick coupled with low price is expected to make the fly ash brick popular with contractors and builders, who are the main customers of bricks.

Figure 1. Fly ash bricks compacted in laboratory by using a Baldwin Hydraulic Press. (Note that the fly ash used for the bricks shown in the above photo is high-grade Class C fly ash.)

Previous research conducted at the University of Missouri-Columbia [6, 8] showed that fly ash can be compacted into bricks and other cylindrical shapes, which upon curing can be as strong as ordinary fired clay bricks and concrete bricks. However, the freeze-thaw property of the fly ash bricks was lacking, only able to pass about 8 instead of 50 freeze-thaw cycles as required by the ASTM standard for fired clay bricks [6]. The purpose of this project is to improve the freeze-thaw property of the fly ash brick substantially, so that it can pass the 50 cycles required by ASTM for fired clay bricks.

Nine different methods to improve the free-thaw property of the fly ash brick have been tested in this Phase I project, including: (1) use of an optimum fly-ash-to-water ratio to make the brick, (2) use of a higher compaction pressure than used before, (3) use of longer curing time, (4) better mixing and mold vibration to enhance consolidation in mold prior to compaction, (4) use of a split mold instead of a single-piece mold for compaction, (5) adding nylon fiber to the fly ash prior to compaction, (6) adding Portland cement to the fly ash prior to compaction, (7) adding hydrated lime to the fly ash prior to compaction, (8) using sealants to reduce water absorption of the fly ash brick, which in turn reduces the freeze-thaw forces, and (9) adding a small amount of a chemical that causes air entrainment in the fly ash brick.

This research to solve the freeze/thaw problem of the compacted fly ash brick is sponsored by the National Science Foundation (NSF) as a Small Business Innovation Research (SBIR) Phase I project. The project started on July 1, 2005, and will end in May 2005. Most of the planned experiments have been completed by now (March 2005); some will continue until the end of May 2005. As will be shown from the data presented here, the objective of finding one or more than one way to solve the freeze/thaw problem has been accomplished successfully.

2. EXPERIMENTAL METHOD

This study used the Class C fly ash produced by the Thomas Hill Power Plant in north-central Missouri, a power plant owned by the Associated Electric Cooperative Inc. (AECI) – the nation's largest electric cooperative. The Thomas Hill Power Plant receives its coal from Wyoming by train. The coal is a low-sulfur coal of the subbituminous type, and the fly ash generated from the coal is Class C, having approximate 27% lime (CaO), which is the main cementing agent in the fly ash. Having high concentration of CaO is a key characteristic that distinguishes the Class C fly ash from the Class F fly ash. Depending on the boiler (burner) used, two types of fly ash are generated at the Thomas Hill Plant: the "high-grade fly ash" which is generated by pulverized-coal boilers, and the "low-grade fly ash" which is generated by cyclone boilers. The high-grade ash contains little (less than 0.1 %) unburned carbon, and has a light brown color. In contrast, the low-grade fly ash has close to 10% unburned carbon, and is dark gray. Due to this color difference in the ashes, the bricks produced also have different natural colors: light brown for the bricks made of the high-grade fly ash (see Figure 1), and dark gray for the bricks made of the low-grade fly ash. No attempt has been made at this stage of the research to alter the color of the bricks by using coloring pigments.

The hydraulic press used for compacting fly ash bricks in this study is the Baldwin Press that can generate a maximum force of 30 tons. The fly ash was mixed with water by using a semi-automatic stand mixer (KitchenAid Bowl Lift Stand Mixer, Model Professional 5 Plus). Then the mixture was fed into the mold – both a full-mold and a half-mold were used. Upon compaction, the brick (or half-brick if half-mold was used) was removed from the mold and placed in a curing chamber. After curing at room temperature, bricks are either placed inside the automatic free-thaw chamber for the freeze/thaw test, or dried in an oven for the drying test. Note that drying is needed for testing the water absorption properties of the fly ash brick. The freeze/thaw test, the drying test and the water immersion test were all done according to ASTM standard for ordinary clay bricks [9].

3. TEST RESULTS

Extensive experimentation has been conducted in this study not only to determine the freeze/thaw properties, but also certain other properties of the fly ash bricks including density, water absorption, compressive strength and saturation coefficient. However, in consistent with the title of this paper, only the freeze/thaw test results will be reported in detail. Results of the other tests will be mentioned only in passing.

3.1 Preliminary work to improve process

At the beginning of this study, an effort was made through some screening tests to determine the optimal fly-ash-to-water ratio (F/W ratio), and the optimum method for mixing the fly ash with water. It was found that the F/W ratios used for making bricks in a previous study [8], 9.0 for the high-grade fly ash and 5.67 for the low-grade fly ash, are not the optimum. Stronger bricks can be made at F/W = 7.0 for the high-grade and at F/W = 4.0 for the low-grade. Once this was determined, all the subsequent tests for fly ash without additive were conducted with F/W ratio of 7.0 for the high-grade fly ash, and 4.0 for the low-grade fly ash.

Effective and uniform mixing of fly ash with water is an important condition for producing good quality fly ash bricks. Initially, the study used a hand-held kitchen mixer to mix the fly ash with water, the same as that done in the two previous laboratory studies [6] and [8]. However, soon it was discovered that the quality of mixing by using handheld mixers is poor and inconsistent; it depends on the skill and care of the experimenter. Therefore, a semi-automatic stand mixer (KitchenAid Bowl Lift Stand Mixer, Model Professional 5 Plus) was purchased and used, which provided better and more consistent mixing. Still, this is for small batch laboratory mixing. The best equipment for providing effective and efficient mixing in commercial mass production may be quite different, which forms a topic of future investigation.

3.2 Testing the effect of additives (fiber, cement and lime)

The effects of adding a small amount of fiber, cement or lime on the freeze-thaw resistance of the fly ash bricks were tested. The results are tabulated in Table 1. For each of the 11 test runs in Table 1, five half-bricks were used. Note that ASTM standard [9] requires the use of half bricks for not only the freeze-thaw test but also the water absorption tests and the unconfined compressive strength test. Therefore, all the bricks tested are half-bricks of the standard size 4" (Width) x 4"(Length) x 2.1"(Depth). For each of the 11 runs, three full bricks of 4" (Width) x 8" (Length) x 2.1" (Depth) were compacted under the same condition. Upon curing, each was sawed into two halves and used as two test specimens, with each specimen having a square surface area of 4" x 4". Five specimens were used for each test run in Table 1; the 6th half brick of each set was saved for testing water absorption and unconfined compressive strength.

Table 1. Experiment Set No. 1: Manual Freeze/thaw test result of flyash bricks compacted at low pressure (1,830 psi). (Purpose: To see if low pressure compaction and 2-week curing are sufficient to produce durable bricks. **Test Conditions**: Used a full-brick mold with bricks pushed out of mold.)

Set 1 Run No.	Fly Ash Grade[1]	Flyash-to-Water Ratio	Fiber Cont. (unit)[2]	Cement Cont. (%)[3]	Lime Cont. (%)[4]	Curing Period (day)	Freeze/Thaw Cycles[5]		Remark
							Crack[6]	Failure[7]	
1	H	7.0	0	0	0	15	4	15	Failed in 6 to 29 cycles
3	L	4.0	0	0	0	15	25	31	4 of 5 passed 50 cycles with damage
5	H	7.0	1	0	0	15	4	9	All failed in 8 to 10 cycles

6	H	7.0	5	0	0	15	7	>50	At the end, all broke into pieces but held together by fiber
9	H	6.22**	0	0	5	14	6	8	All 6 failed in 6 to 9 cycles (worst set)
10	H	6.22**	0	5	0	14	5	>50	4 of 5 passed 50 cycles with loss of skin layers and edges
11	L	4.0	1	0	0	17	13	49	4 of 5 passed 50 cycles with little minor damage
12	L	4.0	5	0	0	14	24	>50	2 cracked in the first two cycles but did not break in 50 cycles.
15	L	3.81**	0	0	5	14	6	8	All failed in 7 to 8 cycles
16	L	3.81**	0	5	0	14	11	17	All failed in 11 to 37 cycles
27	H	7.0	0	0	0	13	4	6	Dough-like mixture

Note: 1. H for high-grade and L for low-grade.
2. Each unit of fiber is equivalent to using 1 pound of nylon fiber in one cubic yard of fly ash, which is approximately equivalent to 0.1 % concentration by weight.
3. Cement concentration is the dry weight of Portland cement divided by the combined dry weight of the fly ash and cement, in %.
4. Lime concentration is the dry weight of the hydrated lime divided by the combined dry weight of the fly ash and lime, in %.
5. Numbers of freeze-thaw cycles cited are based on the average of 5 test specimen.
6. Cycle that visible large crack starts.
7. Cycle that the brick lost more than 5% weight or broke up completely.

** Additional water was added for the cases with cement and lime, resulting in a wetter mixture than without additives.

Summary of freeze-thaw cycles passed:

	Average	Range	Stand. Dev.
High-grade fly ash:	**23**	**6-50+**	**19.3**
Low-grade fly ash:	**35**	**8-50+**	**18.6**

The effect of adding fiber[1] to bricks made of high-grade fly ash can be seen from comparing the results of Run 1 (without fiber or other additive) with Run 5 and 6 (with respectively 1 and 5 units of fiber). It can be seen that without fiber (Run 1), the average of five samples started to develop cracks in as short as 4 cycles, and failed in15 cycles. In contrast, with 1 unit of fiber (Run 5), the samples started to crack in 4 cycles, and failed in 9 cycles; with 5 unit of fiber (Run 6), the bricks started to crack in 7 cycles, but the bricks passed 50-cycles without falling apart – cracked parts were held together by the fiber. The result shows that for the bricks made of high-grade fly ash, adding only 1 unit of fiber has questionable value on the freeze-thaw resistance of the fly ash bricks, whereas adding 5 units of fiber shows a clear advantage. Note that the literature on the website [10] of the manufacturer of this nylon fiber indicates that 3 or more units of the fiber is required to yield a secondary reinforcement for concrete, which appears to be consistent with the amount needed for enhancing the freeze-thaw property of the fly ash brick.

[1] The fiber used in this study, type RC nylon fiber produced by the NyCon Inc., is sold commercially for use in fiber reinforced concrete. Each "unit" of fiber corresponds to one pound of fiber in one cubic yard of concrete, or one cubic yard of the fly ash bricks in our case, which corresponds to about 0.15% of the weight of the brick.

For the low-grade fly ash bricks, those without fiber or another additive (Run 3) started to develop crack in 25 cycles and failed in 31 cycles. In contrast, those with 1 unit of fiber (Run 11) started to crack in 13 cycles, and 4 out of 5 passed 50 cycles without failure, and those with 5 units of fiber started to crack in 24 cycles and passed the 50 cycle test. This shows that putting fiber in low-grade fly ash bricks is also effective in enhancing the freeze-thaw property of the bricks, especially if 5 units of fiber are used.

The effect of adding hydrated lime was a surprise; it had no beneficial effect to bricks made of either type of the fly ash. For instance, for Run 9 which is the case for adding 5% lime to high-grade fly ash, the bricks started to crack in 6 cycles, and failed in 8 cycles, as compared to 4 and 15 cycles, respectively, for the control group (i.e., Run 1, without additive). For the Run 15 which is the case for adding 5% lime to low-grade fly ash, the bricks cracked in 6 cycles and failed in 8 cycles, as compared to 25 cycles for crack and 31 cycles for failure of the corresponding case without using lime – Run 3.

The effect of adding Portland cement to fly ash in making bricks was studied in Run 10 (5% cement in high-grade fly ash) and Run 16 (5% cement in low-grade fly ash). For Run 10, all the 5 samples had either initial or early cracks, but 4 out of 5 lasted for 50 cycles or more with only skin damage – the cores were intact. The skin damage is likely due to the presence of water at the brick surfaces during compaction, which greatly increased the local values of the fly-ash-to-water ratio at the surface of the bricks. During this run, it was observed that over 100 grams of dilute mixture was squeezed out during compaction, proving that too much water was used for this run. For the bricks made in Run 16, crack initiated in 11 cycles, and the bricks failed in 17 cycles, showing a worse result than the corresponding case without cement – Run 3. Based on this study, it can be seen that while adding cement to the low-grade fly ash appears to have questionable value, adding cement to the high grade fly ash appears to help, especially if an appropriate solids-to-water ratio, greater than 6.22, is used.

Note that the bricks reported in Table 1 were made of the same kinds of fly ash and compacted at the same compaction pressure as those in a previous study [6]. Since the bricks in the previous study survived only 8 freeze-thaw cycles whereas most of the bricks in Table 1 passed more than 37 cycles, sufficient progress has been made in this first round of tests of this study. Some of the bricks that passed the 50-cycle freeze-thaw with minor surface damages are shown in Figure 2.

(a) Low-grade fly ash with fiber (b) High-grade fly ash with fiber

Figure 2. Samples of half-bricks upon completion of 50 cycles of freeze-thaw tests.

3.3 Test of the effect of sealants

It was envisioned that by using a suitable liquid sealant, the porosity of the fly ash brick can be reduced, resulting in reduced water absorption, which in turn may reduce the damage caused by freeze-thaw. Consequently, three types of sealants have been tested: A (CONSPEC), B (StoneTech X2), and C (Degussa), with results shown in Table 2.

Table 2. Manual Freeze/thaw test of flyash bricks treated with sealants. (Purpose: To test the effect of sealant on the freeze-thaw property of fly ash brick. **Test Conditions**: Low compaction pressure of 1,830 psi, and no fiber, cement or lime in fly ash.)

Brick No. (Set 1)	Fly Ash Grade	Flyash-to-Water Ratio	Sealant Type[1]	Sealant Appl. Method	Curing Period (day)	Freeze/Thaw Cycles[2]		Remark
						Crack	Failure	
21-1-1	H	7.0	A	Brush 15 min.	21	no	26	Broke in 2 large pieces
21-2-2	H	7.0	A	Dip 15 min.	21	27	>50	Thin layer peeled off surfaces
21-3-1	H	7.0	B	Dip 10 min.	21	31	35	Broke into 4 pieces
21-3-2	H	7.0	B	Dip 30 min.	21	38	>50	Thin layer peeled off surfaces
21-1-2	H	7.0	B	Dip 24 hrs.	21	23	42	Broke in 2 large pieces
21-2-1	H	7.0	B	Dip 24 hrs.	21	30	46	Broke in 3 large pieces
28-2-1	L	4.0	A	Dip 30 min.	14	no	36	Skin started to peel off after 31 cycles
28-2-2	L	4.0	A	Dip 10 min.	14	no	42	Skin started to peel off after 27 cycles
28-3-1	L	4.0	B	Dip 10 min.	14	no	27	Large surface layer are corner fell off
28-3-2	L	4.0	B	Dip 30 min	14	no	27	Broke into pieces
28-1-1	L	4.0	B	Dip 24 hrs.	14	21	25	Large and deep cracks, almost broke apart
28-1-2	L	4.0	B	Dip 24 hrs.	14	21	25	One side broke apart, front face still good
27-2-1	H	7.0	C	Brush twice	44	41	>50	Coating dissolved and edge suffered damage in 41 cycles

Note: 1. Type A sealant is CONSPEC, type B sealant is StoneTech X2, and type C sealant is Degussa color cure obtained from Midwest Block and Brick.
2. Cycles cited are for each brick (one speciment).

Summary of freeze-thaw cycles passed:

	Average	Range	Stand. Dev.
High-grade fly ash:	**43**	**26-50+**	**8.5**
Low-grade fly ash:	**30**	**25-42**	**6.4**

Comparing the freeze-thaw cycles of the bricks listed in Table 2 with those listed in Table 1 shows that the sealants benefited the bricks made of high grade fly ash, whereas it had questionable value for bricks made of low grade fly ash. When properly used, both sealants A and B (respectively for Runs 21-2-2 and 21-3-2) resulted in high-grade-fly-ash bricks that passed the 50-cycle freeze-thaw test. It is of interest to note that these two runs that passed the 50 cycles used fly ash bricks dipped in the sealant for 10 to 30 minutes. Dipping for a much longer time of 24 hours (e.g., Runs 28-1-1 and 28-1.2) was counter-productive.

3.4 Effect of compaction pressure

It is known from previous studies that higher compaction pressures result in denser and stronger fly ash bricks and other compacted objects [6, 8]. Therefore, it seems reasonable to assume that by using higher compaction pressure, the bricks produced will also be able to pass higher freeze-thaw cycles than those produced at lower pressures. A set of experiments was conducted to bear this out, and to see whether by doubling the compaction pressure of the bricks from those of Set 1, the resultant bricks can endure many more freeze-thaw cycles than those of Set 1. This was the motivation for Set 2A tests given in Table 3. However, as can be seen from the results in Table 3, the opposite was found: both the high-grade and the low-grade fly ash bricks compacted at the higher pressure of 3,660 psi failed in significantly fewer cycles than those for the bricks compacted at the lower pressure of 1,830 psi. This surprising result is believed to be caused at least in part by the change in the freeze-thaw test method, rather than in the weakness of the higher-pressure bricks.

It should be realized that the first set of experiments, with results listed in Table 1, was conducted by using manual freeze-thaw. This, according to ASTM Standard C67 [9], requires placing the bricks in a tray containing water of 0.5-inch depth, entering the tray with the bricks into a freezer, allowing the bricks to freeze to 16^{o}F, and then taking the tray out the freezer and allowing the bricks and the water in the tray to thaw gradually in the laboratory until all the water in the tray has melted and the brick temperature has reached 60^{o}F. It was an elaborate procedure that could be done only one cycle per working day and no cycles performed over weekends and holidays. It took typically 65 days to complete one set of freeze-thaw tests. Adding two weeks for curing the bricks, the first set of experiments (those reported in Table 1) took approximately 80 days to complete. Because the NSF project was intended for 6 months only and because several sequential sets of data are needed to have a good understanding of the freeze-thaw problem, it was decided after the first set of experiments that the freeze-thaw test method must be automated. Note that ASTM standard was designed for manual freeze-thaw at the frequency of one cycle per day, but it allows automatic freeze-thaw as well if conducted appropriately.

Automatic freeze-thaw was implemented in this project by placing electric heat cables around the metal tray containing bricks in 0.5 inch of water, and allowing the bricks and ice in the tray to thaw in the freezer by electric heating. The freeze-thaw cycles were controlled by a PLC (Programmable Logic Controller), which in turn used a thermocouple imbedded in a dummy brick in a tray with the fly ash bricks. By using such a system, initially we were able to speed up the freeze-thaw to 5 cycles a day. Soon it was learned that the fast cycles of the automatic freeze-thaw caused severe thermal stresses (thermal shocks) to the bricks, not accounted for by the ASTM Standard. The standard was intended to simulate more or less the stresses caused by gradual freezing and gradual thawing as occurring in nature in winter. It does not account for sharp change of temperature, and large temperature gradients that can generate large stresses to damage the bricks during improper freeze-thaw in the laboratory.

Table 3. Experiment Set No.2A: Freeze/thaw test result of fly ash half bricks compacted at high pressure (3,660 psi) and ejected by push-out. (Initial use of automatic freeze-thaw). (Purpose: To determine whether a doubling of compaction pressure will result in better bricks in terms of freeze-thaw property. **Test Conditions:** Curing period: 2 weeks; no additive used.)

Brick No. (Set 2A)	Fly Ash Grade	Flyash-to-Water Ratio	Mold[1] Insert	Freeze/Thaw Cycles		Remark
				Crack	Failure	
1-1	H	7.0	no	7	7	Had problem separating brick from bottom plate
1-2	H	7.0	no	7	7	Brick had surface damage (cavities) upon ejection
2-1	L	4.0	no	14	14	Brick had surface damage (cavities) upon ejection
2-2	L	4.0	no	14	14	Problem with automatic thaw noticed (overheating)
3-2	L	4.0	S	--	44	Brick had smooth surfaces upon ejection
4-1	H	7.0	S	14	14	Brick had surface damage (cavities) upon ejection
4-2	H	7.0	S	14	14	Brick had surface damage (cavities) upon ejection
4-3	H	7.0	no	44	>50	Brick had surface damage (cavities) upon ejection
4-4	H	7.0	no	14	14	No mixing; 3min. gravity infiltration; poor brick
4-5	H	7.0	L	13	13	No mixing; 3min. gravity infiltration; poor brick made

Note: 1. Two PVC piston insets were made to reduce the amount of fly ash squeezed out the mold and to produce stronger strength at corners and edges. "L" is for the larger PVC insert; "S" is for the smaller PVC inset, and "no" is without inset.

Summary of freeze-thaw cycles passed:

	Average	Range	Stan. Dev.
High-grade fly ash:	**17**	**7-50+**	**13.8**
Low-grade fly ash:	**24**	**14-44**	**14.1**

One thing observed during our initial use of the automatic freeze-thaw equipment was an ice island that remained in the center of the tray during the last stage of thawing. This caused the faces of the bricks in the tray that face outside to have a much higher temperature than the opposite faces, thereby generating a large temperature gradient across the bricks. This often caused the brick to break in layers. This problem was solved by covering the bottom of the trays with a thick layer of insulation, which resulted in more uniform heating of water and the bricks in the tray. Another thermal shock was found during freezing. Trays of bricks placed on the top shelves of the standing freezer were subjected to a blast of freezing air during the freezing stage. During the initial stage of the freezing when the bricks are still warm, the blast of freezing air on the warm brick surface causes large thermal stresses that produce surface cracks. This problem was solved by not using the top shelf. However, the data taken reported in Table 3 were all affected by these thermal shocks, and hence are not reliable. This explains the abnormality of the test results. A price paid for solving the thermal shock problem is that the improvements slowed down the automatic freeze-thaw to 3 cycles per day.

After the thermal shock problems have been corrected, a set of data was taken under the same conditions of those in Table 3. The result is given in Table 4. A significant improvement has been accomplished, as can be seen from the fact that the average cycles passed by the high-grade and low-grade fly ash bricks are now respectively 31 and 29 cycles, as compared to 17 and 24 in the previous case. This provided evidence that the thermal shock was the cause of poor data in the initial use of the automatic freeze-thaw equipment.

Table 4. Experiment Set No.2B: Freeze/thaw test result of fly ash half bricks compacted at high pressure (3,675 psi) and ejected by push-out. (Improved automatic freeze-thaw). (**Purpose**: To determine whether a doubling of compaction pressure from 1,830 to 3,660 psi will result in better bricks in terms of freeze-thaw property. **Test Conditions:** No additive was used except for bricks 9-1 and 9-2, which had 5 units of fiber; and the initial problem with automatic freeze-thaw was corrected (improved) by adding more insulation to cover the heating trays.)

Brick No. (Set 2B)	Fly Ash Grade	Flyash-to-Water Ratio	Mold Insert	Curing Period (day)	Freeze/Thaw Cycles		Remark
					Crack	Failure	
5-1	L	4.0	L	15	--	14	Brick had surface damage (cavities) upon ejection
5-2	L	4.0	L	15	28	28	Corner layer broke off upon ejection
5-3	L	4.0	no	15	28	28	Minor surface damages (cavities) upon ejection
6-1	H	7.0	no	15	--	29	Ditto
6-2	H	7.0	no	15	--	29	Ditto; used PAM
6-3	H	7.0	L	14	-	29	Ditto
6-4	H	7.0	L	14	--	29	Do damage upon ejection; used PAM and plastic bottom sheet
7-1	L	4.0	no	18	19	28	Some damage and a crack upon ej. Did not use PAM
7-2	L	no	19	18	19	28	Minor surface damage upon ejection
8-1	H	7.0	L	17	19	>50	Brick had no damage upon ejection
8-2	H	7.0	L	17	19	>50	Ditto
9-1*	L	4.0	no	17	28	>50	Ditto
9-2*	L	<4.0	no	17	19	28	Mixer stopped; had to add more water.
10-1	H	7.0	L	14	15	15	Excess water squeezed out
10-2	H	7.0	L	14	--	20	Brick sticked to plastic sheet

10-3	L	4.0	no	14	19	31	--
10-4	L	4.0	no	14	28	28	Slight corner damage upon ejection

* Runs with 5 units of nylon fiber.

Summary of freeze-thaw cycles passed:

	Average	Range	Stan. Dev.
High-grade fly ash:	**31**	**15-50+**	**11.8**
Low-grade fly ash:	**29**	**14-50+**	**8.7**

3.5 Test of split molds

In previous studies of coal compaction [11-13], it was found that coal compacts are often damaged while being ejected from the mold by an advancing piston. The damage is caused by tensile stress concentration at and near the sharp corner of the inner edge of the mold as illustrated in part (a) of Figure 2. Due to this damage, coal logs made of a split mold (i.e., dislodging the coal logs from the mold by split-opening the mold) were shown to be far superior to those made from a push-out mold [13].

Based on the foregoing result of coal log compaction research, it was decided in this project to test a split mold in order to see whether it can make better fly ash bricks. Tests were performed by comparing the bricks made by pushing the brick out of a sharp-edged mold with bricks made by using a split mold. A split mold is a specially designed mold made in pieces joined together by bolts. Upon compaction of any brick, the mold can be opened up (split) by disassembling the mold. This can avoid the push-out ejection of bricks. If damage due to what is shown in Figure 2 (a) exists, the fly ash bricks made from a split mold would be significantly better than those made from a push-out mold. The test results from the split mold A is shown in Table 5.

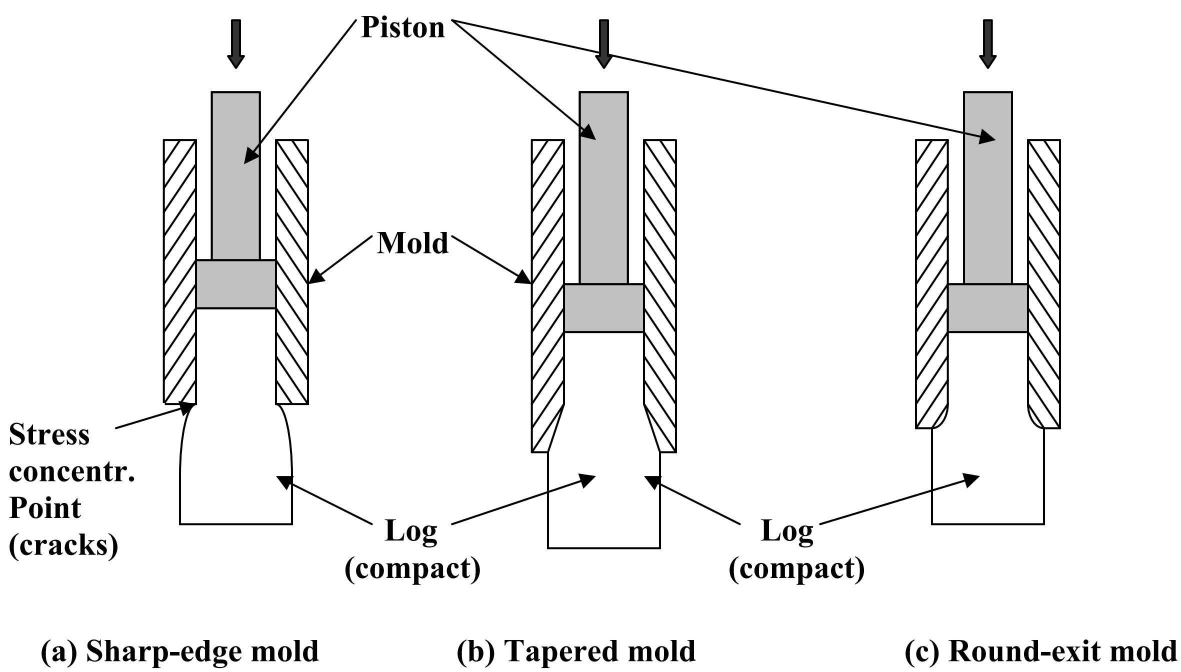

Figure 2 Mold exit shapes and crack formation during log (compact) ejection

Table 5. Experiment Set No.3: Freeze/thaw test results of fly ash half bricks compacted at high pressure (3,675 psi) and ejected by uniform split mold. (Improved automatic freeze-thaw). (Purpose: The purpose of this set of tests is to determine whether a uniform split mold can produce better bricks in terms of freeze-thaw property. **Test Conditions:** Use of split mold A made by technician Kirk)

Brick No. (Set 3)	Fly Ash Grade	Flyash-to-Water Ratio	Add-Itive[1]	Curing Period (day)			Freeze/Thaw Cycles		Remark
				In cure Cham.	In Water	Total Cure	Crack	Failure	
11-1	H	7.0	no	12	2	14	6	6	Manual thaw on Dec.25 done in a rush
11-2	H	7.0	no	11	2	13	12	12	Automatic freeze- thaw
12-1	L	4.0	no	10	2	12	36	36	Manual thaw
12-2	L	4.0	no	10	2	12	22	22	Automatic freeze-thaw
13-1	H	7.0	F5	10	9	19	14	45	Severe surface cracks in 41 cycles
13-2	H	7.0	F5	10	9	19	45	>50	
14-1	L	4.0	F5	9	9	18	32	45	
14-2	L	4.0	F5	9	9	18	27	32	
15-1	H	7.0	C5	9	9	18	10	10	
15-2	H	7.0	C5	9	9	18	10	10	
16-1	H	7.0	no	--	--	15	--	14	Curing time includes 10 hrs. of pressure boiling
16-2	H	7.0	no	--	--	15	--	14	Ditto
16-3	H	4.0	no	--	--	15	--	14	Ditto

Comparing the results in Table 5 (for split mold) with the data in Table 4 (for push-out mold) indicates that the split mold did not produce bricks that can endure longer freeze-thaw cycles, contrary to original expectation. This can be explained, however, in hindsight. The sharp-corner damage phenomenon shown in Figure 2 (a) is valid only for brittle materials such as coal. Because fly ash mixed with water is far more ductile than coal particles, and is compacted at a pressure 4 times lower than the pressure for compacting coal logs, the sharp exit corner of brick molds have little effect on the brick quality. Beside, in extruding (pushing out) the newly compacted bricks from the mold, intense shear stress due to friction is generated at the surface of the brick, which enhances the surface strength of the brick produced, in a way similar to extruded products.

3.6 Hot-water curing of fly ash bricks

From a previous study by Hu [8], it is known that the curing of fly ash is slower than the curing of concrete products. For instance, by compacting fly ash logs (i.e., cylindrical test samples) at 5,000 psi, Hu found that upon 14 days of curing the unconfined compressive strength of logs was approximately 6,960 psi, whereas upon 60 days of curing the strength increased to

11,020 psi, which represents a 58 % increase. It was thought that the process of longer curing might be hastened by boiling cured bricks in water. This was tested by first curing four samples (two high-grade and two low-grade fly ash bricks) in the curing chamber for 15 days, followed by boiling the samples in a pressure cooker for 10 hours, before they went through the freeze-thaw test. As can be seen from the results in Table 6, all the four samples of the test bricks failed in 14 cycles of freeze-thaw. This shows that the 10 hours of hot-water boiling did not help to enhance the freeze/thaw resistance of the bricks in any noticeable way. In fact, thermal stresses may have been introduced during the boiling which weakened the bricks. This test result does not rule out other heating methods to enhance curing, such as steam curing, which will be tested in the future.

Table 6. Experiment on high-pressure boiling of fly ash bricks. (Purpose: To determine whether boiling fly ash bricks at high temperature in a pressure cooker can speed up curing and enhance the performance of the bricks. **Test Conditions**: Bricks were make of fly ash without additive and compacted at low pressure (1,838 psi) using the Type B split mold made by technician Rex; the bricks were all cured for 15 days including 10 hours of pressure cooking at 230 ^{o}F, approximately.)

Brick No. (Set 3B)	Fly Ash Grade	Flyash- to-Water Ratio	Freeze-Thaw Cycles		Remarks
			Crack	Failure	
16-1	H	7.0	--	14	
16-2	H	4.0	--	14	
16-3	L	7.0	--	14	
16-4	L	4.0	--	14	

Summary of freeze-thaw cycles passed:

	Average	Range	Stan. Dev.
High-grade fly ash:	**14**	**14-14**	**0**
Low-grade fly ash:	**14**	**14-14**	**0**

3.7 Effect of Longer Curing Time

Previous study has shown that by increasing the curing time from 2 weeks to 60 days, the compressive strength of compacted fly ash bricks increases by bout 50%. Will this increase in the compressive strength result in an increase in the freeze/thaw resistance of the log or bricks? This was tested in Set.4 experiments, and the results are listed in Table 7.

Table 7. Experiment Set No.4: Freeze/thaw test results of fly ash half bricks compacted at low pressure (1780 psi) and cured for 60 days. No additives were used. (Purpose: The purpose of this set of tests is to determine whether 60-day curing improves the freeze-thaw property of the fly ash bricks, and whether split mold can produce better bricks than push-out mold.)

Brick No. (Set 4)	Fly Ash Grade	Flyash- to-Water Ratio	Mold-Type	Freeze-Thaw Cycles		Remarks
				Crack	Failure	
1-1	H	7.0	Split	9	9	
1-2	H	7.0	Split	9	9	

1-5	H	7.0	Push-out	9	9	
1-6	H	7.0	Push-out	9	9	

It can be seen from Table 7 that all the bricks that were cured 60 days failed in as short as 9 cycles, and it is the same for split mold as it is for the push-out mold. Comparing with the bricks listed in Table 6, which were cured for only 15 days, it shows that longer curing has no beneficial effect on the freeze/thaw property of fly ash bricks.

3.8 Use of Air-Entrainment to Enhance the Freeze/Thaw Property of Fly Ash Bricks

An air-entrainment chemical, used normally for air-entrained concrete, was tested for its effectiveness in increasing the freeze/thaw property of the fly ash bricks. As can be seen from Table 8, it had a remarkable effect on improving the freeze/thaw property of the fly ash bricks. The air entrainment made high-grade fly ash bricks to pass the 50-cycle freeze/thaw test without any crack or significant damage to the bricks, and it made the low-grade fly ash bricks to pass 40 cycles of the test without any crack or damage. This appears to be the most effective single method to improve the freeze/thaw property of the fly ash brick, and the most economic method. Only 0.2% of the chemical by weight was used, and the chemical was readily soluble in the water used for wetting the fly ash. Thus, using this chemical does not add significant work or cost to the process.

Table 8. Experiment Set No.6: Freeze/thaw test results of fly ash half bricks compacted at low pressure (1780 psi) and cured for 15 days. Air-entrainment chemical of 0.2% by weight was used. (Purpose: to determine the effectiveness of using an air-entrainment chemical, manufactured by the W. R. Grace Company, on the freeze/thaw resistance of the fly ash bricks.)

Brick No. (Set 6)	Fly Ash Grade	Flyash-to-Water Ratio	Mold-Type	Freeze-Thaw Cycles		Remarks
				Crack	Failure	
1-3	H	7.0	Push-out	>50	>50	
1-4	H	7.0	Push-out	>50	>50	
2-3	L	4.0	Push-out	40	45	
2-4	L	4.0	Push-out	40	45	

4. CONCLUSION

While some of the methods tested, such as using an optimum fly-ash-to-water ratio, using higher compaction pressure, using longer curing time, and adding Portland cement to the fly ash, were found to increase the compressive strength the of the fly ash bricks, they are all ineffective in improving the freeze-thaw property of the fly ash bricks. The reason that they improve the compressive strength but not the freeze/thaw property is that crack formation and damage of bricks are due to the development of tensile stress instead of the compressive stress in bricks. Besides, as the compressive strength of the brick increases, the brick becomes more brittle (less ductile), which makes it more susceptible to cracking and freeze/thaw damage.

This study found that the most effective and practical (economical) method to enhance the freeze/thaw property of the fly ash bricks is the use of an air-entrainment chemical. By adding only 0.2% of the air-entrainment chemical by weight, the bricks made of high-grade fly ash can already pass the 50-cycle ASTM standard, and the bricks made of low-grade fly ash can pass 40 cycles of the test. Tests are currently underway to run more extensive tests of the air-entrainment method, such as using more than 0.2% of the chemical, to see if it can make the low-grade fly ash bricks to pass the 50-cycle standard. Other measures, such as using nylon fiber, also were found to be effective in enhancing the freeze/thaw property of the fly ash bricks. However, they are not as effective as using air-entrainment chemicals.

Finally, since the objective of this NSF sponsored research is to solve the freeze/thaw problem of the fly ash bricks, it is gratifying to know that this problem has been solved by using air-entrainment, in much the same way it is used in air-entrained concrete.

5. ACKNOWLEDGMENT

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