

Environmental Properties of Fly Ash Bricks

Henry Liu¹, Shankha K. Banerji², William J. Burkett¹ and Jesse VanEngelenhoven¹

¹Freight Pipeline Company, 2601 Maguire Blvd., Columbia, MO. 65201, USA

²University of Missouri-Columbia, Civil & Environmental Engineering Department, Columbia, MO. 65211, USA

KEYWORDS: brick, carbonation, CO₂ sequestration, environmental properties, fly ash brick, leaching, mercury emission, radon emission, TCLP test

ABSTRACT

Research conducted at Freight Pipeline Company (FPC) sponsored by the National Science Foundation (NSF) has found that fly ash bricks made by compacting Class C fly ash have excellent structural properties including freeze-thaw resistance, compressive strength, flexure strength, shear strength, and bonding strength, matching those of ordinary clay bricks and concrete bricks. The compacted fly ash bricks also pass ASTM C62 requirements for clay bricks used for buildings in Severe Weather (SW) regions. However, because fly ash normally contains a small amount of pollutants including heavy metals, it was important to determine whether the bricks made from fly ash would release pollutants into the environment when being used on buildings, when stored on construction sites, and when buildings are demolished and the bricks are reused or disposed of in landfills.

Four most critical environmental concerns about building products made from fly ash are: (1) potential for mercury vapor emission from the products, (2) potential for radon emission from the products, (3) potential for leaching pollutants (heavy metals) from such products into ground caused by rain, and (4) potential for polluting landfills when a building is demolished and the broken fly ash products enter landfills. Each of these four concerns has been tested in laboratory for the compacted fly ash bricks. The test results showed that: (1) Fly ash bricks made from Class C fly ash do not emit mercury into air. On the contrary, they adsorb mercury from air, making the ambient air cleaner. (2) Fly ash bricks do emit radon gas, but only at about 50% of that emitted from concrete. Thus, if it is considered safe to use concrete or concrete products in buildings, it should be even safer to use fly ash bricks. (3) Leaching of pollutants from fly ash bricks caused by rain is negligible. (4) Fly ash bricks pass the EPA-mandated TCLP test easily, and hence are "non-hazardous" for landfilling or handling.

In addition, long-term observation of the compacted fly ash bricks revealed that the long-term growth of strength of fly ash bricks is due to carbonation caused by absorption of CO₂ from the atmosphere. This means use of fly ash bricks causes sequestration of CO₂ from the atmosphere, bringing relief to global warming.

This study was conducted using fly ash bricks compacted from a Class C fly ash resulting from burning a Powder River Basin Coal. Whether the results would hold also for bricks made from other fly ashes, or for fly ash products other than compacted bricks, remains to be seen through future research.

INTRODUCTION

For more than two decades, researchers [1-11]¹ have been trying to use either fly ash as the only solid, or fly ash in combination with other solids such as cement, lime, bottom ash, sand, reservoir sediment, etc., to make bricks and/or other building products such as blocks, pavers, etc. Generally, two fundamentally different approaches exist to make brick and other building products. The first is to make bricks in the same way fired clay bricks are made except for the use of fly ash to substitute for a portion of the clay or the entire amount of clay used in making bricks. Examples of this approach are Chow [7], and Kayali [11]. This approach requires the newly shaped (extruded or compacted) bricks to be heated in kilns fired to over 2,000 °F, which consumes much energy (normally in the form of fossil fuel), and pollutes air and contributes to global warming. The second approach, which relies on the self-cementing property of Class C fly ashes, or fly ashes that contain a large amount of calcium, do not need to fire or heat the products in kilns. Instead, the products can be cured in the same way concrete is cured – by keeping the products in a wet environment for more than 24 hours until the material sets and hardens due to chemical reaction with the water or moisture contained in the products – the hydration reaction. Hereafter, fly ash bricks and products made by this second approach will be referred to as “**non-fired**” fly ash bricks and products.

Prior to 2002 [6], no researcher mentioned or reported any test of the freeze-thaw property of fly ash bricks. In 2002, Li and Lin [6] were the first to report testing the freeze-thaw properties of fly ash bricks. Using a high-grade Class C fly ash produced from burning Powder River Basin Coal, with the ash containing as much as 25% CaO and less than 0.5% LOI (loss-on-ignition), they were able to make very strong non-fired fly ash bricks, having compressive strength in the neighborhood of 5,000 psi. However, they reported that the bricks made could pass only an average of 7 freeze-thaw cycles in a laboratory test conducted according to ASTM C67 [12], whereas ASTM requires that building bricks used in places that freeze in winter must pass a minimum of 50 cycles [13]. Without being freeze-thaw resistant, non-fired fly ash bricks could not be used in most areas of the United States and in any nation or regions that freeze in winter. Even though Li and Lin identified the freeze-thaw problem of non-fired fly ash bricks, they did not solve the problem nor suggested how to solve the problem. It was not until 2005 that Liu, under a National Science Foundation (NSF) research grant [9, 10], tackled and solved the freeze-thaw problem of the non-fired fly ash bricks. The test results of this NSF sponsored study formed the basis of a U.S. patent application [14], a PCT (Patent Cooperation Treaty) application [15], a European application [16], and patent filing in 8 nations including China [17].

Analysis conducted by the Green Brick Company [18] has shown that non-fired fly ash bricks can be made at a cost 10 to 20% less than that of fired fly ash bricks, using less than 10% of the energy used by fired fly ash bricks [19]. In what follows, only non-fired fly ash bricks will be discussed. Unless otherwise mentioned, whenever we use the term “**fly ash brick**” in the following discussion, it refers only to **non-fired** fly ash bricks.

¹ Numerals in [] represent corresponding items in REFERENCES.

The purpose of this paper is to describe a set of tests conducted to determine the environmental properties of fly ash bricks. The tests were part of the NSF Phase 2 project on fly ash bricks [20], under **Task 6 Test Possible Environmental Concerns**. Four different experiments were conducted: (1) mercury emission, (2) radon emission, (3) leachate of pollutants caused by rain, and (4) TCLP test. They are described in the next section.

EXPERIMENTS

1. Mercury Emission Test

The purpose of this test was to determine the amount of mercury emission from fly ash brick, and to see if such emission would impact the environment and the health of building occupants. Mercury was singled out for testing/analysis not only due to the danger of mercury to health but also because it is the only heavy metal present in fly ash in liquid form, which can evaporate and cause potential health problems.

Before presenting the test results on mercury emission, some perspectives are in order. It should be realized that mercury and other heavy metals are present everywhere in the environment – in the air that we breathe, the water that we drink, the food that we eat, and the things that we use and come to contact with, including building products. Nothing in this imperfect world is completely free of mercury and other pollutants. Therefore, our concern should not be whether there is any mercury and other pollutants in fly ash products, but rather whether the pollutants that exist in the product can leach out or be emitted from the product in any way or quantity that can cause safety problems, or that exceeds safety limits.

In the case of mercury, the outdoor air that we breathe contains mercury of variable amounts depending on location, altitude and time. For instance, the website of the Wisconsin Department of Natural Resources (WDNR) [21] reports that the average ambient background concentration of mercury in the air of Wisconsin is 1 to 2 Ng/m³ (nanograms of mercury per cubic meter of air), and the State's legal limit for mercury in air is 0.3 µg/m³ (microgram of mercury per cubic meter of air), which is equivalent to 300 Ng/m³. In contrast, a study conducted in New Jersey [22] found that in a community where mercury is used for cultural purpose, the outdoor mercury vapor averaged about 5 Ng/m³, whereas the indoor level was about 25 Ng/m³. According to OSHA standard [23], the maximum level of exposure to mercury vapor by workers on 8-hour shifts is limited to 0.1 mg/m³ (milligram per cubic meter). This is equivalent to continuous exposure of 0.0333 mg/m³, or 33.3 µg/m³ (microgram per cubic meter). Finally, Section 3 of the EPA Mercury Response Guidebook gives the safe value for continuous exposure (Level 3 Action) as 1 µg/m³ [24]. In the current study to evaluate the safety of mercury emission from fly ash bricks, the EPA limit of 1 µg/m³ was used.

Using the EPA limiting value of 1 µg/m³, and using ASHRAE (American Society of Heating, Refrigeration, and Air-Conditioning Engineers) Standard which requires that residential buildings must have a minimum air exchange rate of 0.25 change per hour [25], the following equation was derived [26]:

$$F = 0.25 \frac{V_o}{A} \dots\dots\dots (1)$$

In Eq. 1, F is the mercury vapor emission flux of the fly ash bricks in $\mu\text{g}/\text{h}/\text{m}^2$ (micrograms per hour per square meter); V_o is the air volume in the house (the same as the interior volume of the house) in m^3 (cubic meter); and A is the total surface area of the brick emitting mercury in m^2 (square meter).

For a house having a floor plan of 100 ft by 30 ft and a height of 10 ft, if all the 4 exterior walls and the floor are made of fly ash bricks facing inside (i.e., with fly ash bricks in contact with the indoor air), Eq. 1 reduces to $F = 0.41 \mu\text{g}/\text{h}/\text{m}^2$. Due to the unusually large amount of fly ash bricks used indoors for this building, and due to the use of Eq. 1 which is based on the conservative value of $1 \mu\text{g}/\text{m}^3$ given by EPA and the conservative value of 0.25 exchange per hour, the value of $F = 0.41 \mu\text{g}/\text{m}^2/\text{h}$ calculated above is very safe. Therefore, to determine whether mercury emission from fly ash bricks is safe or not, all that we need to do is to measure the emission rate F from laboratory tests, and to see whether it is greater or smaller than $0.41 \mu\text{g}/\text{m}^2/\text{h}$. If the measured emission rate is smaller than $0.41 \mu\text{g}/\text{m}^2/\text{h}$, then the emission of mercury from fly ash brick is considered safe and vice versa. This explains the approach used to evaluate the safety of mercury emission from fly ash bricks using laboratory data.

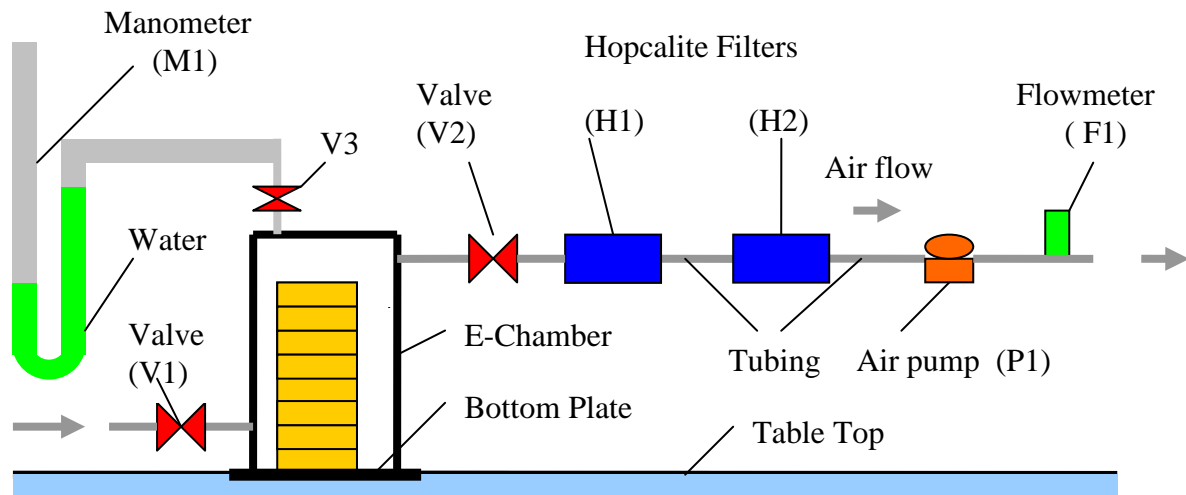


Figure 1 Experimental system for measuring mercury vapor emission from fly ash bricks

The dynamic flux method based on mass balance was used to determine the mercury flux emission from fly ash bricks. The bricks tested were placed in an environmental chamber (E-chamber) as shown in Figure 1. The chamber, being a rectangular box made of transparent polycarbonate plates of $\frac{1}{4}$ " (6.4 mm) thickness. The outer dimensions of the chamber are: 24" (height) x 24" (length) x 12" (width). The internal volume of the chamber is approximately 3.76 ft^3 (0.107 m^3). Due to the expected small amount of emission from each fly ash brick, for accuracy of the experiment a total of 40

fly ash bricks were placed in the E-chamber for testing. Each brick had the dimensions of 8" (length) x 4" (width) x 2" (depth). The bricks were stacked in 5 adjoining columns with 8 bricks in each column – see Figure 1. Hopcalite filters were used to measure the mercury concentration of the air exiting the E-chamber with and without the 40 bricks, and the mercury concentration of the ambient air was also measured by using Hopcalite filters. The test was continued for 7 days so that enough mercury can be accumulated on the filters to yield reliable measurements. From such measurements, the flux rate F was calculated. More details of the test are published in [26] and hence not repeated here.

This test found that the F value was approximately -0.081 Ng/h/m^2 . The fact that the F value was negative means that the fly ash bricks not only did not emit any mercury, they actually adsorbed mercury that existed in the inflow air (ambient air). The fact that fly ash bricks adsorb instead of emit mercury is comforting news. This means when such bricks are used in the future, not only will they not pollute ambient air, they actually will make the ambient air slightly cleaner for people to breathe. In a research sponsored by EPRI (Electric Power Research Institute), Gustin and Ladwig reported in 2004 that practically all fly ashes derived from burning subbituminous coals adsorbed instead of released mercury during their tests [27]. Since the fly ash bricks used in our mercury emission/absorption study were made from PRB coal which is subbituminous, our finding that F is negative or the fly ash bricks adsorb instead of emit mercury is consistent with what was reported in [27] for fly ash. Note that the negative F values measured for fly ashes from subbituminous coal, reported in Table 2 of [27], are in the range of 1 to 100 Ng/h/m^2 . This is 10 to 1,000 times larger than what we measured in this research for fly ash bricks. The fact that fly ash bricks adsorb much less mercury than individual fly ash particles do is to be expected, due to the low permeability or hydraulic conductivity of fly ash brick, and the much smaller surface-to-volume ratio for bricks than for loose fly ash particles.

2. Radon Emission Test

Radon is a radioactive gas that can cause lung cancer. According to the U.S. Environmental Protection Agency (EPA), radon is the second leading cause of lung cancer, responsible for about 21,000 lung cancer deaths every year in the U.S. The higher the concentration of radon is in the air that we breathe, and the longer that we breathe such air, the higher the risk is for us to get lung cancer.

Radon (Rn), atomic number of 222, has a single parent called radium (Ra), which is a radioactive solid with atomic number 226. Both radon and radium have the common ancestor – uranium (U) (atomic number 238). According to accepted theory, uranium (U 238) has a half-life time of 4.5 billion years. After several generations of decay lasting 4.5 billion years, U238 is turned into radium (Ra 226) which has a half-life time of 1,600 years. Then it transforms into radon (Rn 222) which has a half-life time of only 3.82 days before it turns into other isotopes and finally into stable lead (Pb) in 23 years (half life).

Even though radon has a half-life time of only 3.82 days, it is dangerous to people because it is in gaseous form and permeates into the surface layer of the atmosphere and enters buildings through doors, windows, and building cracks. Because uranium exists in all rocks, soil and ground water, the ground water under the surface of the earth is rich in both radium and radon gas. Because the radon gas is much lighter than water, it rises through ground water table and permeates through soil to reach the atmosphere or enter houses through building cracks, especially basement cracks. Generally, the radon level in buildings, especially in basement areas, is higher than that in the outdoor atmosphere. The outdoor concentration of radon in the atmosphere is approximately 0.4 pCi/L (pico curies per liter), and the indoor concentration of radon is usually 2 to 3 times higher. Whenever the radon gas inside a building reaches or exceeds 4 pCi/L, EPA regards it as being unhealthy for long-term exposure and recommends immediate remedial action to be taken, such as evacuating the building, venting the indoor air that has high radon concentration, sealing basement cracks, or venting the space beneath basement floors. Thus, 4 pCi/L is usually referred to as the “**action level**” of radon gas for buildings.

According to U.S. Geological Survey [27], the average concentration of uranium 238 in U.S. coal, common shale, granitic rock, fly ash, black shale and phosphate rock is respectively 1.5, 4.5, 6.0, 15, 18 and 60 ppm (parts per million by weight). This shows that fly ash in the U.S. contains on the average approximately 15 ppm or 10 times the amount of uranium contained in coal, and one-fifth of the amount of uranium contained in phosphate rock.

In this NSF research project on fly ash bricks, the radon gas emission test was conducted by testing fly ash bricks placed inside two sealed containers of different sizes – a large container of 24”(H) x 24”(L) x 12”(W), and a small container of 14”(L) x 10”(W) x 7”(H). Both containers were made of transparent plastic, so that the radon meter placed inside each container can be read from outside. Radon meters were placed both outside and inside the containers, so that both the ambient level and the inside-the-container level of radon concentration can be read separately. Subtracting the outside level from the inside level yields the radon concentration caused by the bricks.

The fly ash bricks used in the test were made from the fly ash resulting from burning PRB coal. A sample of the fly ash was tested by an outside laboratory² to determine the concentration of uranium in the fly ash. It was found that the sample contained 9.96 ppm of uranium. This shows that the fly ash used in making our test bricks contained about 50% less uranium than that of the average fly ash in the United States.

(a) Large container test – For the large containers, 40 bricks were placed inside the container in the same manner as shown in Figure 1 for the mercury vapor emission test.

² The sample was tested at University of Missouri-Columbia’s Nuclear Reactor Center under supervision of Dr. William Miller, Professor of Nuclear Engineering. Gamma Ray Spectroscopy Analysis was performed to determine the concentration of U238.

A radon meter was also placed inside the container before the container was sealed with duct tape, to monitor the radon concentration in the container as a function of time. The same test was conducted separately by using fly ash bricks and concrete bricks of approximately the same size, so that the radon emission level of the fly ash bricks can be compared with that of the concrete bricks. Each fly ash brick had a weight of 2,116 g, and a surface area of 727 cm²; each concrete brick had a weight of 2143 g, and a surface area of 669 cm². This means that the weight of the fly ash brick is about 1.3% smaller than that of the concrete brick, and the surface area of the fly ash brick is about 8% larger than the area of each concrete brick.

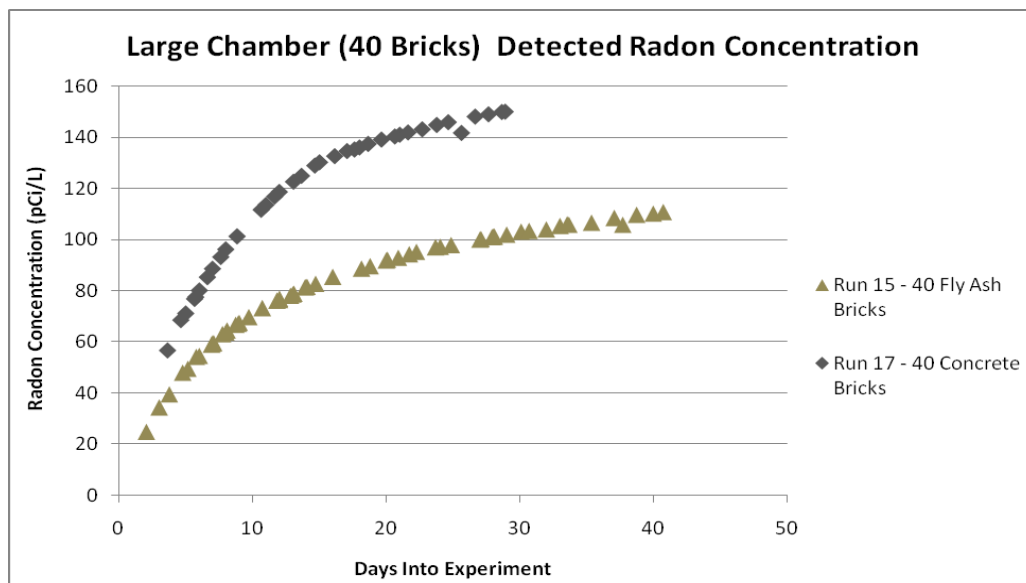


Figure 2. Increase in radon concentration in large container with test time for 40 bricks

From Figure 2, it can be seen that for both the concrete bricks and the fly ash bricks, the radon concentration increased with time, and it gradually leveled off after about 40 to 50 days. The graph also shows that the fly ash bricks emit radon about 50% less than concrete bricks do.

(b) Small container tests --

As can be seen from Figure 2, when the large container was used for testing, it took more than 30 days for each test to reach a steady state or equilibrium value of radon concentration in the container. Therefore, for studying the variation of the equilibrium value of radon trapped in a sealed container with other parameters, such as the surface area of the of the fly ash bricks inside the container, a smaller container was needed so the experiment could be completed within weeks instead of months. As can be seen from Figure 3, with the use of the small container, equilibrium values of the radon concentration in the container can be reached within 10 days.

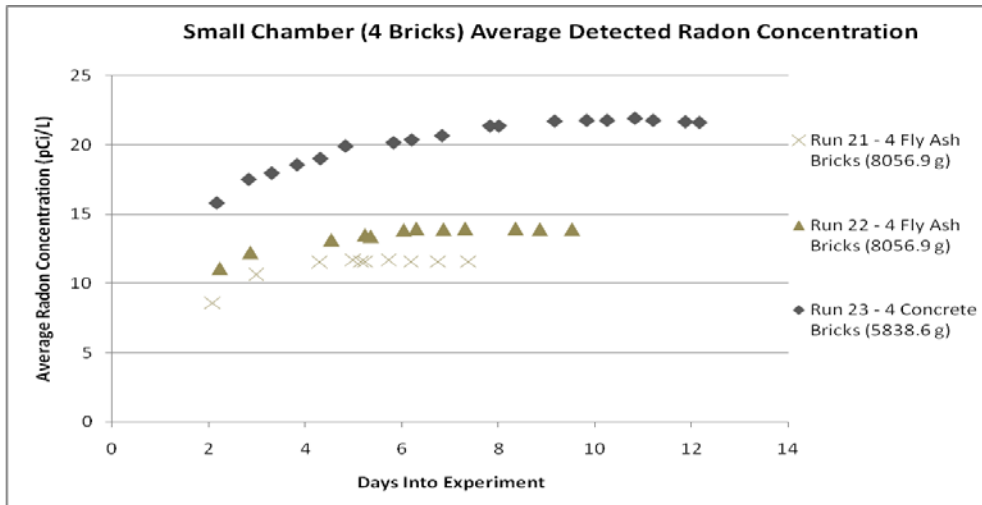


Figure 3. Increase in radon concentration in small container with test time for 4 bricks

It was anticipated that the equilibrium amount of the radon gas trapped inside a tank is linearly proportional to the total surface area of the fly ash bricks within the tank. This hypothesis was checked by conducting the same experiment 4 times, using fly ash bricks of 4 different areas, 562, 654, 1155 and 1717 cm^2 . If the foregoing hypothesis is correct, then by dividing the total amount of radon measured in each case by the total surface area of the brick, the resultant value of radon per unit brick area, in the unit of pCi/cm^2 , will be constant independent of the brick surface area used. As can be seen from Figure 4, this value appears to be the same for all four brick surface areas tested, thereby proving the validity of the hypothesis. This experiment shows that the amount of radon gas emitted from fly ash bricks is proportional to the surface area rather than the weight of the brick.

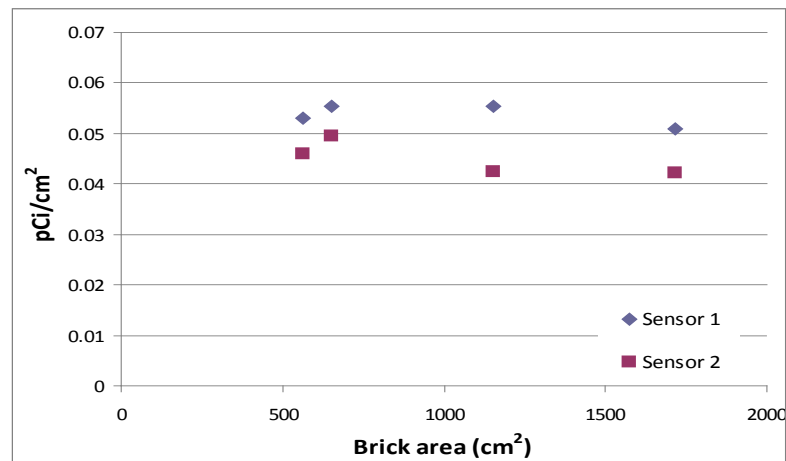


Figure 4. Radon emitted from unit area of fly ash bricks for tests conducted with bricks of 4 different areas

An experiment was also carried out by placing a layer of dry powdered fly ash of approximately 40 mm thickness inside a rectangular tray of 283 mm length, 229 mm width and 65 mm height. The tray containing the fly ash was placed in the same small container that measured the radon emitted from the bricks. Then the container was

sealed and the radon gas concentration was monitored for several days. In as short as 3 days, the radon concentration reading reached a steady-state value of approximately 1.4 pCi/L. Then, water was added into the tray until the entire surface of fly ash in the tray was submerged under about 10 mm of water. Then, the container was sealed again and the radon measurement re-started. In as short as 3 days, again the steady state was reached with a reading of 6.0 pCi/L. This means by submersing fly ash under water, the radon emission from the ash has increased by approximately 4 times. This is interesting because fly ash is oftentimes mixed with water to form slurry for disposal in a slurry pond or reservoir. This test shows that by doing so, approximately 4 times more radon is released into the atmosphere than that emitted from dry powdered fly ash having the same surface area in contact with the atmosphere. This test result should not be misinterpreted as suggesting that wet disposal of fly ash is worse than dry disposal of fly ash. Wet disposal prevents fly ash from being blown into the air by wind, thereby eliminating a potent air pollution problem that can be caused by dry disposal of fly ash.

3. Leachate Resulting from Rain

Because most fly ash bricks will be used outdoors, such as face bricks for buildings and pavers for walkways and so on, they will be exposed to rains. Therefore, a fair question to ask is whether such exposure to rain will cause a significant amount of pollutants such as heavy metals to leach out from the bricks, causing pollution to groundwater, surface water and/or soil.

A search of literature revealed no standard or accepted method for testing the effect of rain on pollutant leachate from bricks. Therefore, the writers had to develop their own method for the study. Initially, a plan was developed to test the effect of rain by subjecting the fly ash bricks to artificial rains generated by spraying water from a shower nozzle on bricks at different angles and intensities over different durations. While such an experiment will certainly yield interesting results, it would consume a great deal of time and money from the project, yet it would not provide proof that leachate of pollutants from bricks caused by rains is insignificant. Due to this, a much simpler rain simulation test was devised and performed in this study. The simulation test involved immersing a standard size fly ash brick of 8" x 4" x 2.25" in a 10-gallon-size aquarium tank filled with distilled water – see Figure 5. The tank had dimensions of 500mm (L) x 254mm (W) x 305mm (H). Aeration is introduced by bubbling air into the bottom of the tank so that the distilled water is soon saturated with air including carbon dioxide, which affects the pH of the water. By doing so, the chemical property of the distilled water in the tank is expected to be similar to that of rain water. Also, bubbling air through the water in the tank causes turbulence and water circulation in the tank, which in turn causes large mass transfer at the brick surface and hence large release of pollutants from the bricks, yielding conservative results.

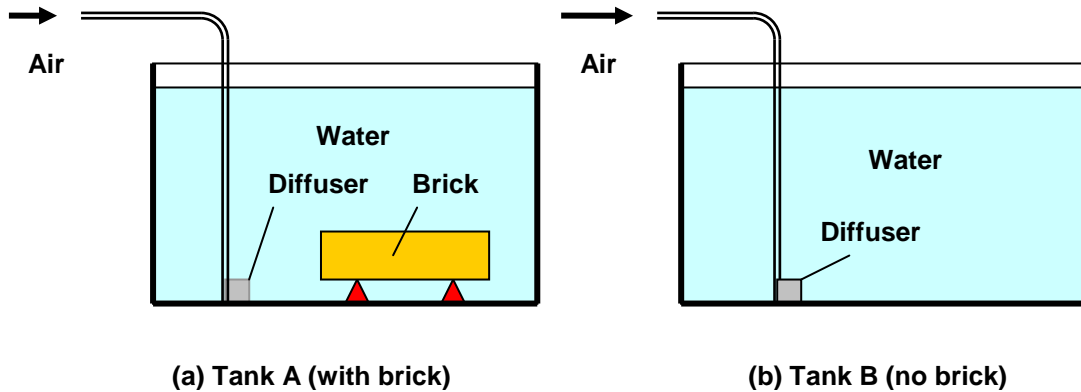


Figure 5. Apparatus for testing simulated rain water leachate from brick

As shown in Figure 4, two identical tanks were used for the test, one with brick (**A**), and one without brick (**B**). The one without brick gives background values of pH and pollutants in the water without presence of the brick. The brick tested had a mass of 2.08 kg, and the water used was 8.25 gal. The water to solid (brick) weight ratio used in tank A was 15 to 1, which is more conservative than the 20:1 ratio used in the TCLP (toxicity characteristic leaching procedure) recommended by EPA (U.S. Environmental Protection Agency).

Both tanks were aerated with an air stone diffuser and an air pump for 30 minutes prior to the start of the test to dissolve CO_2 from air to simulate rain water. The pH of the water of both tanks was measured at the start of the test. The concentration of total solids in the water in ppm was measured using a conductivity probe. The tanks were continuously aerated for 5 days with any loss of water due to evaporation made up by adding distilled water to maintain the set volume. The test ended after 5 days. Samples of water were collected at 0 hr, 20 hr and 120 hr. The samples were sent for metal analyses to a local laboratory (Laboratory & Environmental Testing, Incorporated, Columbia, MO). The metals measured include Hg, Cd, Cr, Ag, Ni, As, Ba, Pb, Se, and Zn. Total conductivity and pH of the water was also measured at 0 and 120 hr.

The pH of the water samples in Tanks A and B at time 0 hr (30 min after aeration) were 5.6 and 5.5. Normal pH of rainwater is around 5.6 so the water was simulating rain water quite effectively [29]. The pH of the tank waters after 5 days (120 hr) were 8.20 for Tank A and 6.72 for Tank B. The increase of pH in Tank B was unexpected as there was no brick in the tank to interact with the acidic water, but possibly the air stone or plastic tubing could affect pH since there was no buffering capacity in the water. The pH of the Tank A was higher which would be caused by the dissolution of basic materials from the brick surface. Thus rainwater falling on the fly ash bricks would be neutralized to some extent depending on the contact time, which would be beneficial.

The conductivity (in terms of total dissolved solid, TDS) of the water samples in Tanks A and B at time 0 hr were 2.0 ppm and 1.4 ppm respectively. This would indicate that the distilled water used had low level of dissolved solids present. However, in reality rain water does contain some (less than 12 ppm) TDS [30], so the water used was simulating rainwater to a large extent. The TDS values in the tank waters after 5 days were: 94.5 ppm for Tank A and 2.6 ppm for Tank B. These results validate the pH increase in these tanks as components of fly ash bricks from surface were being dissolved into the water in Tank A. The slight increase in TDS in Tank B also indicates some dissolution of ions from the diffuser or tank materials. The chemical test results will clarify what was being dissolved into the water.

The chemical tests consisting of metal analyses were conducted on the 5 water samples from the two tanks. Samples 1 and 4 were from Tank B (without brick) at time 0 hr and 120 hr (5 days), respectively. Samples 2, 3 and 5 were from Tank A (with brick) at 0 hr, 20 hr and 120 hr. Table 1 shows the results of chemical analyses. Table 1 also provides the U.S. Environmental Protection Agency (EPA) drinking water standards for the metals in question. In addition the EPA Toxicity Characteristic Leaching Procedure (TCLP) heavy metal limits are also included in the table for comparison purposes.

From Table 1, it can be seen that as expected both the 0 hr samples had very low concentrations of chemicals. The chemical in trace quantities present at 0 hr were : aluminum, calcium, barium, potassium, magnesium, sodium, strontium and zinc. The concentration levels of these metals in distilled water were insignificant as expected. They constituted the total dissolved solids mentioned earlier. The concentration levels of these metals were slightly higher in the tank with the brick (Tank A, Sample 2) even at time 0 hr as contact with brick caused some rapid dissolution of these ingredients.

The Tank without brick (Tank B) had some minor increase in chemical constituents (as evidenced by an increase in TDS) after 5 days indicating some dissolution of chemicals from the aeration device or tank materials. However, these increases were not significant. The major interest is the chemical constituent's results of Tank A with time. It can be seen that many constituents increased progressively with time. After 5 days as indicated earlier by the TDS tests, the increase in aluminum, barium, calcium, chromium, potassium, magnesium, molybdenum, sodium, sulfur, strontium, vanadium and zinc occurred in the tank water. This would be expected as the acidic rain water was neutralized by the basic brick but some soluble salts dissolved to a very limited extent in the water.

It is important to note that none of these metal concentrations exceeded the EPA drinking water limits. Thus the rain water will not cause any significant leaching of toxic metals from the bricks. The soaking of the brick in simulated rainwater for 5 days was an extreme test as normally the rain water would run down the bricks for limited time period without such complete contact as in the test.

Table 1. Chemical Analyses on Water Samples from Tanks A & B. (Sample numbers are listed below the time periods; all results are in mg/L.)

Constituents Sample No.	Tank B		Tank A			EPA Drinking Water Standards	EPA TCLP Test limits (D list)+
	0 hr 1	120 hr 4	0 hr 2	20 hr 3	120 hr 5		
Ag	<0.005	<0.005	<0.005	<0.005	<0.005	NS	5.0
Al	0.02	0.02	0.17	0.78	1.9	NS	NS
As	<0.05	<0.05	<0.05	<0.05	<0.05	0.01	5.0
B	<0.05	<0.05	<0.05	0.1	0.38	NS	NS
Ba	0.001	0.001	.0062	0.078	0.192	2.0	100.0
Be	<0.001	<0.001	<0.001	<0.001	<0.001	NS	NS
Ca	0.1	0.44	0.27	6.07	17.5	NS	NS
Cd	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.005	1.0
Cr	<0.002	<0.002	<0.002	0.014	0.04	0.1	5.0
Cu	<0.002	<0.002	<0.002	<0.002	0.002	1.3*	NS
Fe	<0.02	<0.02	<0.02	<0.02	<0.02	NS	NS
Hg	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.002	0.2
K	0.1	0.1	<0.1	0.66	1.2	NS	NS
Mg	0.01	0.02	0.035	0.28	0.62	NS	NS
Mn	<0.002	<0.002	<0.002	<0.002	<0.002	NS	NS
Mo	<0.005	<0.005	<0.005	0.01	0.034	NS	NS
Na	0.3	0.3	0.6	5.7	13.0	NS	NS
Ni	<0.002	<0.002	<0.002	<0.002	<0.002	0.1	NS
P	<0.07	<0.07	<0.07	<0.07	<0.07	NS	NS
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	0.015*	5.0
S	<0.04	<0.04	0.18	5.05	10.2	NS	NS
Se	<0.05	<0.05	<0.05	<0.05	<0.05	0.05	1.0
Sr	0.001	0.001	0.0072	0.164	0.518	NS	NS
V	<0.001	<0.001	<0.001	0.002	0.0048	NS	NS
Zn	0.003	0.005	0.003	<0.003	0.004	NS	NS

*Cu and Pb concentrations are action limits measured at consumer tap, corrosion protection must be provided where concentrations are exceeded

NS- No standards

+ Reference: <http://www.ehso.com/cssepa/TCLP.htm>

Note: The QA/QC for all the above data is available.

4. TCLP Test Results:

TCLP test represents a condition when the fly ash bricks after use may be disposed of in a sanitary landfill where household solid waste is also present. Under these conditions the fermentation and anaerobic breakdown of organic wastes produces organic acids which mainly consists of acetic acid. The TCLP test requires that the

materials that are being tested are crushed to sizes less than 9.5 mm size (3/8 in). The crushed solids are then contacted with acetic acid at appropriate pH for 18 ± 2 hr in a rotary contactor at a temperature of 23 ± 2 °C. After the leaching process, the filtrate is subjected to chemical analyses to determine its quality in terms of heavy metals. The test procedure follows EPA Method 1311 [31].

Five different fly ash bricks were selected for TCLP testing. These bricks were:

1. Thomas Hill Power Plant - high grade-ammoniated flyash brick
2. Thomas Hill Power Plant- high grade- air entrained flyash brick
3. Thomas Hill Power Plant- high grade-colored flyash brick
4. Labadie Power Plant- high grade air entrained flyash brick
5. Thomas Hill Power Plant - low grade air entrained flyash brick.

These bricks were pulverized and passed through a ¼ inch sieve. The materials passing the sieve were used for the TCLP test. This would make the test more rigorous with smaller size having larger surface area and more likely to leach chemicals. The pulverized samples were mailed to a renowned laboratory in St. Louis, MO for conducting the TCLP test. The laboratory was affiliated with Testamerica Laboratories, Inc. They followed the EPA test method 1311 for the TCLP test. The results of the TCLP tests for metal analyses are shown in Table 2. It can be seen that only Barium (Ba) and Chromium (Cr) were present in the leachate from all samples. The other 8 heavy metals were not even detected in any of the 5 fly ash leachates. The concentrations of Ba in the leachates were several orders of magnitude less than the allowable limit of 100 mg/L. In case of Cr the concentrations in the leachate were also more than one order of magnitude less than the EPA allowed limit. **Thus, the fly ash bricks used in these tests can be classified as “non-hazardous materials” in accordance with EPA definition of non-hazardous waste material.**

Table 2. Flyash brick TCLP test results. (All results are in mg/L)

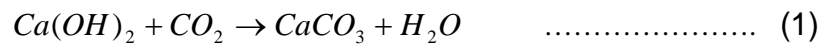
Constituents	Samples					EPA TCLP Test Limits (D List)
	1	2	3	4	5	
Sliver	ND	ND	ND	ND	ND	5.0
Arsenic	ND	ND	ND	ND	ND	5.0
Barium	0.645	0.517	0.655	0.432	0.203	100.0
Cadmium	ND	ND	ND	ND	ND	1.0
Cobalt	ND	ND	ND	ND	ND	NS
Chromium	0.239	0.115	0.093	0.182	0.013	5.0
Copper	ND	ND	ND	ND	ND	NS
Lead	ND	ND	ND	ND	ND	5.0
Selenium	ND	ND	ND	ND	ND	1.0
Mercury	ND	ND	ND	ND	ND	0.2

ND – Not detected; NS – No EPA limit set ; NS – No standards set.

Note: QA/QC for the data presented is available.

5. Carbon Sequestration

Long-term observation of fly ash bricks indicated that after several years from the time the bricks were made, the surface of the brick hardens into a rock-like or marble-like surface. Such hard surface makes the bricks less permeable to water absorption, and increases the compressive strength and the freeze-thaw resistance of the bricks. For instance, when fly ash bricks were first made without using air-entrainment agent, the bricks passed fewer than 10 cycles of freeze-thaw tested according to ASTM C67 [12]. However, when such bricks were tested 6 years later, all of them passed 50 cycles, meeting ASTM C62 requirements on freeze-thaw resistance of building bricks used in severe weather (SW) regions [13]. It is believed that part of this long-term brick hardening process is caused by **carbonation**, a process well-known in the field of concrete. Carbonation is the process in which the $\text{Ca}(\text{OH})_2$ that exists in concrete reacts with the CO_2 in the atmosphere, causing CaCO_3 (limestone or marble) to be formed according to the following chemical reaction formula:



Because bricks made from Class C fly ash also contains $\text{Ca}(\text{OH})_2$, the same carbonation process that happens with concrete also is expected to happen with fly ash bricks.

What is nice about the carbonation process is that it not only makes fly ash bricks stronger, harder and more freeze-thaw resistant with time but also absorbs CO_2 from the atmosphere, causing carbon sequestration.

To prove that carbon sequestration indeed happens, an environmental chamber (E-chamber) was built as shown in Figure 6. A total of 20 half bricks made from Class C fly ash, each having the dimensions of 4" x 4" x 2.2", were placed in the chamber to adsorb (sequester) CO_2 . Air is pumped into the E-chamber by an air pump, and the air upon contact with the bricks, leaves the chamber through an outlet. A CO_2 sensor is placed both at the inlet and the outlet, to measure the CO_2 concentration of both the inlet and the outlet air. If carbon sequestration is actually taking place, the inlet sensor #1 should detect a higher concentration of CO_2 than the outlet sensor #2 does. The rate of CO_2 sequestration can also be determined from the test.

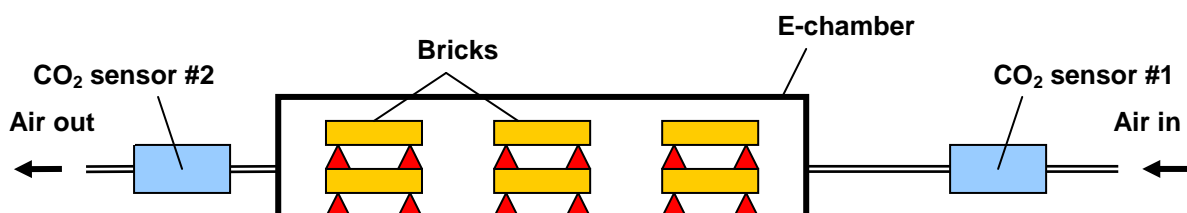


Figure 6. Apparatus for testing carbon sequestration from fly ash bricks

The signals of both the inlet sensor #1 and the outlet sensor #2 are continuously monitored by a computer in the laboratory using the LabView data acquisition software. Testing started in March 2009, and only preliminary test data have been collected so far. As can be seen from Figure 7, as soon as the 20 fly ash half-bricks were placed in the E-chamber and CO₂ recordings started, there was a noticeable decrease of approximately 30% of the CO₂ concentration of the outlet air from the inlet air, showing carbon sequestration by the bricks. Note that zero time corresponds to the time that freshly steam-cured fly ash bricks were placed in the E-chamber and recordings started. The recordings are currently ongoing, and they will be continued for months if not years to see if the rate of carbon sequestration by fly ash bricks decrease with time.

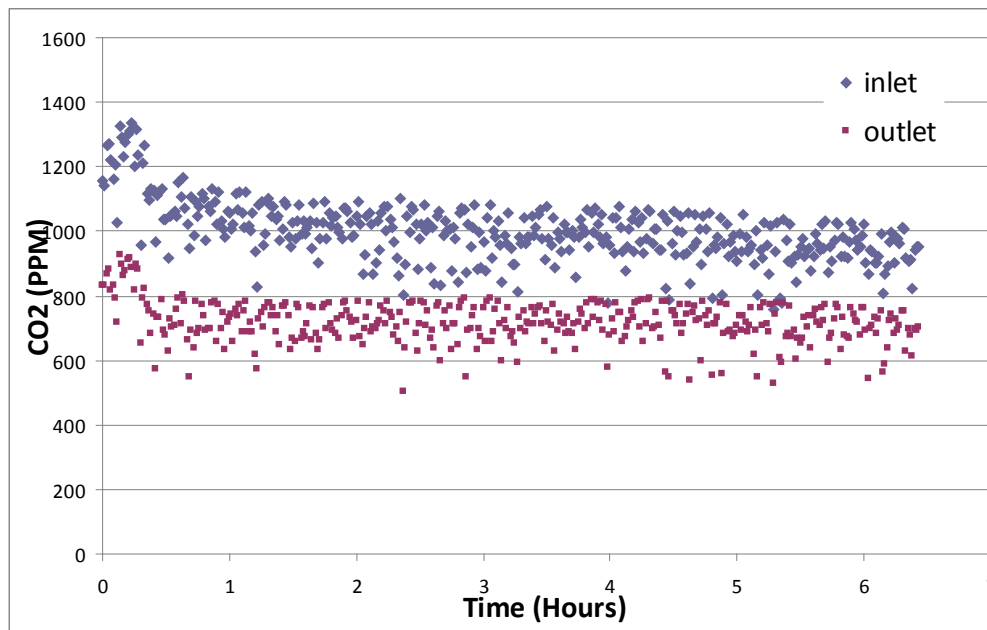


Figure 7. Test of carbon sequestration of fly ash bricks in an environmental chamber at Freight Pipeline Company (FPC).

CONCLUSION

Based on the foregoing test results, the following can be concluded:

1. Fly ash bricks made from Class C fly ash do not emit any mercury at all. On the contrary, they absorb a small amount of mercury from the air in contact with the bricks, making the ambient air slightly cleaner for people to breathe.
2. Fly ash bricks made from Class C fly ash emit radon gas 50% less than radon emitted from concrete.
3. The rate of radon emission from fly ash bricks is linearly proportional to the surface area of the bricks emitting radon.
4. The amount of radon emitted from fly ash submersed in water is approximately 4 times that emitted from dry fly ash covering the same surface area.
5. Rain causes negligible amount of leachate of pollutants (heavy metals) from fly ash bricks. Fly ash bricks immersed in rain water for 5 days causes little pollution to the rain water. The water is still so pure that it passes the EPA standard for

drinking water quality. This should alleviate any concern that fly ash bricks may cause water pollution.

6. Fly ash bricks pass the TCLP test recommended by EPA with large margins. This means that when fly ash bricks are broken and must be disposed of in landfills, they can enter any ordinary landfill for non-hazardous waste materials without any problem.
7. Fly ash bricks can absorb carbon dioxide from the atmosphere in a chemical process called "**carbonation**." This process causes carbon sequestration, reducing the CO₂ in the atmosphere, which helps to mitigate global warming.

ACKNOWLEDGMENT

This study was conducted as a part of the research project sponsored by the National Science Foundation (NSF) under an SBIR (Small Business Innovation Research) Phase 2 research project entitled "Compacting Fly Ash to Make Bricks", NSF Project No. 0548719. NSF support of this project is highly appreciated. The writers also acknowledge advice and services provided by Professor William Miller of the Nuclear Engineering Department of University of Missouri-Columbia, in relation to testing radon gas emission from bricks.

REFERENCES

- [1] Logger, H. (1988), Method for Producing a Building Element from a Fly Ash Comprising Material and Building Element Formed, U.S. Patent No. 4,780,144.
- [2] Kube, S.K. and Palit A. (1995), "Studies in the Developments of Flyash Bricks—An Approach for Cleaner Environment: Part-2," Proc. of the American Power Conference, 57th Annual Meeting, Chicago, 57-1, pp.315-320.
- [3] Riddle, M.S. (1995), Fly Ash Composition and Process for Making Articles therefrom, U.S. Patent No.5,405,441.
- [4] Parsa, J., Munson-McGee, S.H., and Steiner, R.(1996), "Stabilization/Solidification of Hazardous Wastes Using Fly Ash," Journal of Environmental Engineering, 122 (10), pp.935-940.
- [5] Hu, R. S. (2001), High-Pressure Compaction of Fly Ash into Building Materials, M.S. Thesis, Department of Civil and Environmental Engineering, University of Missouri-Columbia, 87 pages. (Adviser: Henry Liu).
- [6] Li, Y. D. and Lin, Y. Y. (2002), Compacting Solid Waste Materials Generated in Missouri to form New Products, Final Technical Report to the Solid Waste Management Program, Missouri Department of Natural Resources (MDNR), Contract No. MDNR 00038-1, submitted by Capsule Pipeline Research Center, University of Missouri-Columbia, 90 pages.

- [7] Chou, M. I. (2003), "Manufacturing Commercial Bricks with Illinois Coal Fly Ash," Proceedings of the World of Coal Ash Conference, Lexington, KY. (Note: This paper is on the Fly Ash Library website www.flyash.info.)
- [8] Hsu, Y. S., Lee, B. J. and Liu, H. (2003), "Mixing Reservoir Sediment with Fly Ash to Make Bricks and Other Products," Proceedings of the World of Coal Ash Conference, Lexington, KY. (Note: This paper is on the Fly Ash Library website www.flyash.info.)
- [9] Liu, H., Burkett, W. J. and Haynes, K. (2005), "Improving Freezing and Thawing Properties of Fly Ash Bricks," Proceedings of the World of Coal Ash Conference, Lexington, Kentucky, 17 pages. (Note: This paper is on the Fly Ash Library website www.flyash.info.)
- [10] Liu, H. (2005), Compacting Fly Ash to Make Bricks, Final Technical Report, NSF-SBIR Phase 1 Project No. DMI-0419311, submitted to NSF, March 2005, 15 pages.
- [11] Kayali, O. (2005), "High Performance Bricks from Fly Ash," Proc. of the World of Coal Ash Conference, Lexington, Kentucky. (Note: This paper is on the Fly Ash Library website www.flyash.info.)
- [12] ASTM (2007), Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile, American Society for Testing and Materials (ASTM), Standard C67, 12 pages.
- [13] ASTM Standard (2005), Standard Specification for Building Brick (Solid Masonry Units From Clay or Shale), American Society for Testing and Materials (ASTM), Standard C62, 4 pages.
- [14] Liu, H. (2006), Method to Produce Durable Non-Vitrified Fly Ash Bricks and Blocks, Non-Provision U.S. Patent Application, No. 11/307023.
- [15] Liu, H. (2006), Method to Produce Durable Non-Vitrified Fly Ash Bricks and Blocks, PCT Application, No. PCT/US06/06314.
- [16] Liu, H. (2006), Method to Produce Durable Non-Vitrified Fly Ash Bricks and Blocks, European Patent Application, No. 06735820.0-1213.
- [17] Liu, H. (2006), Method to Produce Durable Non-Vitrified Fly Ash Bricks and Blocks, Chinese Patent Application No. 200680000117.3.
- [18] Liu, H. and Duckworth, C. (2007), Cost of Flyash Brick Manufacturing at Thomas Hill Power Plant in Missouri, FPC Technical Report, August 15, 2007, 9 pages.
- [19] Liu, H. (2007), Energy in Making Bricks: A Comparison between Clay Bricks and Fly ash Bricks, FPC Technical Report, July 14, 2007, 5 pages.

[20] Liu, H. (2008), Compacting Fly Ash to Make Bricks, Final Report of NSF-SBIR Phase II Project No. 0548719, Technical Narrative: 14 pages.

[21] Wisconsin DNR Website (2009), www.dnr.state.wi.us/toxics/mercury/Mon.

[22] Garetano, G., Gochfeld, M. and Stern, A. H. (2006), "Comparison of Indoor Mercury Vapor in Common Areas of Residential Buildings with Outdoor Levels in a Community Where Mercury is Used for Cultural Purposes," Environmental Health Perspectives, Vol. 114, No. 1.

[23] OSHA website (2007), www.osha.gov/SLTC/mercury/exposure_limits.html

[24] EPA (2001), Mercury Response Guidebook, U. S. Environmental Protection Agency Region 5, prepared for EPA by Tetra Tech EM Inc., Cincinnati, Ohio.

[25] ASHRAE (2004), "Ventilation and Acceptable Indoor Air Quality in Low-Rise Residential Buildings", Standard 62.2, American Society of Heating, Refrigerating and Air Conditioning Engineers.

[26] Liu, H., Banerji, S., Burkett, W. J. and Shinn, M. (2007), "Test of Mercury Vapor Emission from Fly Ash Bricks, Proc. of the World of Coal Ash Conference, Cincinnati, Ohio. (Note: This paper is on the Fly Ash Library website www.flyash.info.)

[27] Gustin, M.S. and Ladwig, K. (2004), "An Assessment of the Significance of Mercury Release from Coal Fly Ash," Journal of the Air & Waste Management Association , Vol. 54 March 2004, pp.320-330.

[28] USGS (2009), Radioactive Elements in Coal and Fly Ash: Abundance, Forms, and Environmental Significance, U.S. Geological Survey Fact Sheet FS-163-97, 5 pages.

[29] McBride, M.B. (1994), Environmental Chemistry of Soils, Oxford University Press, New York.

[30] Laney, R.L., (1965), Comparison of Chemical composition of Rainwater and groundwater in western North Carolina, USGS Professional Paper 525-C.

[31] USEPA (1999) Method 1311- Test Method for Evaluating Solid Wastes, Physical/Chemical Methods, EPA SW-846.