

Test of Mercury Vapor Emission from Flyash Bricks

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KEYWORDS: brick, E-chamber, emission flux, flyash, flyash brick, health concern, Hopcalite, Hopcalite filter, mercury, mercury vapor, test chamber.

ABSTRACT

In 2006, the National Science Foundation (NSF) awarded to Freight Pipeline Company (FPC) a Small Business Innovation Research (SBIR) Phase II grant entitled "Compacting Flyash to Make Bricks." One of the multiple research tasks of this project is to test the emission of mercury vapor from the flyash bricks, in order to determine whether there is significant emission of such vapor from flyash bricks to warrant special attention and mitigation.

The experiment was conducted by placing flyash bricks inside an environmental test chamber (E-chamber). Air was pumped in and out of the chamber at a constant flow rate by using a vacuum pump connected to the outflow of the test chamber. Two Hopcalite filters were connected in series to capture the mercury in the air entering the filters. The amount of mercury captured by the filters was measured to determine the concentration of mercury vapor in the air entering the filter. From this concentration, from the airflow rate, from the duration of the test, and from the brick surface area, the emission flux of mercury from the flyash brick was calculated. The flux was then compared to that is safe according to EPA standard for a typical home having a minimum air change rate of 0.25 per hour. If the flux is less than $0.4\mu\text{g}/\text{h}/\text{m}^2$, it is considered to be safe. To our surprise, the experiments revealed that the mercury flux emitted from flyash bricks was actually negative, meaning that the fly ash bricks not only did not release or emit mercury vapor, they actually adsorbed mercury from the ambient air, rendering the ambient air cleaner than without the bricks.

1. INTRODUCTION

Use of flyash to make bricks helps the environment in the following ways:

- Two-thirds of the flyash generated by power plants in the United States are not used. They are disposed of either in slurry ponds near power

plants, or at mine pits away from power plants. Either way, the disposal is costly to manage for electric utilities, and causes possible water pollution if not handled properly. Use of flyash to make bricks solves this solid waste disposal problem, and turns a waste material into cash for electric utilities.

- Use of flyash bricks reduces the need for using clay bricks and concrete bricks, both of which use fossil fuel and pollute air during their manufacturing process. (Clay bricks must be heated in kilns to over 2,000 °F, which consumes fossil fuel and pollutes air. For concrete bricks and products, they are produced by using cement which in turn uses fossil fuel and pollutes air during the manufacturing of cement.) Because flyash bricks don't use cement and don't need high-temperature heating of bricks in kilns, much energy (from fossil fuel) is saved, and the pollution generated from burning fossil fuel is avoided.
- Because no fossil fuel is burned in making flyash bricks, no CO₂ is generated and no global warming is caused by making flyash bricks. In contrast, the fossil fuel burned in manufacturing clay bricks and in manufacturing cement for concrete bricks are major sources of greenhouse gas and global warming.
- Practically all environmental groups and governments around the world want increased use of flyash to eliminate or reduce land disposal of flyash. For instance, the U. S. Environmental Protection Agency has forged an alliance with other agencies and industry, called "C2P2" program [1]¹, to promote the use of flyash and other coal combustion byproducts.

Notwithstanding the great environmental benefits of using flyash bricks mentioned above, there are concerns in the public and even in the press about the safety of using flyash bricks for buildings, especially when using the bricks indoors. The concern is based on the feeling that flyash being a power-plant waste material must contain some pollutants such as heavy metals (e.g., mercury), which if exceed any safe level, may cause health problems. The writers believe that such concern is unwarranted for the following reasons:

- The amount of hazardous materials (such as mercury and other heavy metals) contained in flyash is normally well within 1 ppm (part per million), which is classified by scientists as "trace substances." The amount of such pollutants is of the same order of magnitude as that found in ordinary soils, concrete and other currently used construction materials.
- Flyash has been used for decades in many other applications such as roadbed, soil conditioner, and concrete mixture. No health or pollution problem, including occupational health problem, has been reported or known for such usages.
- Once made into bricks, the pollutants in the flyash become locked (solidified) inside the bricks, making them even more difficult to escape from the interior of the bricks to cause problems. So, making flyash into bricks must be one of the safest ways to use flyash.

¹ Numerals in [] represent corresponding items in REFERENCES at the end of this paper.

- The Environmental Protection Agency (EPA) classifies flyash as a non-hazardous material.

Even though the health concerns about flyash bricks seem to be unwarranted based upon the above considerations, it is insufficient to deal with or settle this issue based solely on reasoning (such as provided above) and/or expert opinion. Some rigorous scientific experiments and calculations must be carried out to rule out the possibility that flyash bricks may cause health problems. The study reported herein was conducted for such a purpose -- to determine without reasonable doubt that indoor use of flyash bricks will not cause health problems.

2. SCIENTIFIC METHODOLOGY

The scientific methodology used here to prove that flyash bricks don't cause health problem is based on a combination of: laboratory test data on flyash brick emission of mercury vapor, EPA standard on allowable level of mercury vapor in indoor air [2], ASHRAE standard on minimum air change rate for residential buildings [3], and science (logic, math, and physics). By using this methodology and laboratory test data, it is possible to determine scientifically whether there is any significant amount of mercury vapor emitted from flyash bricks, and whether such emission, if any, should cause valid health concerns.

2.1. Mercury Vapor Emission Rate and Flux

The mercury emission rate, R , is defined as the amount of mercury (i.e., the mass of Hg) emitted from the surface of a solid that contains mercury, per unit time. It can be of the unit of $\mu\text{g}/\text{h}$ (microgram per hour)², or Ng/h (nanogram per hour)³. For a flyash brick, the emission rate R from the brick is expected to be a function of the surface area of the brick, the concentration of mercury in the brick, the physical and chemical properties of the brick including but not limited to the permeability, moisture, density and temperature of the brick, and the pressure and temperature of the air around the brick. Wind speed near the surface of the brick is also expected to have an effect on the emission rate.

The mercury emission flux, F , is the mercury emission rate per unit surface area of the brick that emits mercury. A convenient unit for F is $\mu\text{g}/\text{h}/\text{m}^2$. For any flyash brick with uniform composition and mercury content, the mercury emission flux F is assumed to be constant around the brick, and the mercury emission rate from the brick is $R = FA$, where A is the total surface area of the brick in contact with air.

The foregoing definitions of R and F are provided because these quantities will be used in the ensuing calculations.

2.2. Mercury in Air Caused by Indoor Emission from Bricks

Once the mercury emission flux rate, F , has been determined experimentally, one can then use the result to calculate the concentration of mercury vapor

² One microgram (μg) is equal to 10^{-6} gram.

³ One nanogram (Ng) is equal to 10^{-9} gram.

inside any building that uses flyash bricks indoor -- for floors, walls or other usages. This is done as follows:

Suppose that a certain building uses fly ash bricks indoor for floors, walls, and/or other purposes. Suppose the interior volume of the building (i.e., the air volume in the building) is V_o , and the total surface area of the flyash bricks used in the building in contact with the indoor air is A . Because the mercury vapor emission flux of the flyash bricks is F , the total emission rate of mercury vapor from indoor use of flyash bricks is:

$$R = AF \quad \dots\dots\dots (1)$$

If the building is designed to have an *air exchange rate* (also called “air change rate”) of E exchange per hour (1/h), in one hour the building will replace existing indoor air with outdoor fresh air of the amount (volume) of

$$V = E V_o \quad \dots\dots\dots (2)$$

During the same time (i.e., in an hour), the flyash bricks in the building will emit an amount of mercury vapor equal to R , which is given by Eq. 1. Thus, the mean concentration of mercury in the room will be

$$C = \frac{R}{V} = \frac{AF}{E V_o} \quad \dots\dots\dots (3)$$

Equation 3 shows that the mean concentration of mercury vapor in the air inside a house, C , due to the use of fly ash bricks inside the house, can be calculated from the mercury emission flux F , found from the proposed experiment, for any given building having an internal volume of V_o , having an air exchange rate E , and having flyash bricks of total surface area A inside the building.

2.3. Safety from Exposure to Mercury Vapor Emitted from bricks

According to OSHA standard [4], 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). To be on the safe side, one would expect that less than one-third of this value, or 10 µg/m³, should be safe enough for continuous exposure to mercury vapor in home or other residential buildings. However, Section 3 of the EPA Mercury Response Guidebook gives the safe value for continuous exposure (Level 3 Action) as 1 µg/m³ [2]. Therefore, to be on the safe side, we shall use this EPA value of 1 µg/m³ as the threshold level for continuous exposure. Furthermore, ASHRAE (American Society of Heating, Refrigeration, and Air-Conditioning Engineers) recommends that buildings have an air exchange rate of no less than 0.25 change per hour [3]. Using these threshold values of $C = 1 \mu\text{g}/\text{m}^3$ and $E = 0.25$ exchange/h, Eq. 3 yields:

$$F = 0.25 \frac{V_o}{A} \dots\dots\dots (4)$$

It is important to use the correct units for Eq.4, which require V_o to be in m^3 , A in m^2 , and F in $\mu g/h/m^2$. The following example illustrates how Eq. 4 can be used to determine the safety value of F for buildings.

Example 1. A house has 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 flyash bricks facing inside (i.e., with flyash bricks in contact with the indoor air), what is the safe level of emission flux F for this house?

[Solution] For this house, $V_o = 100 \times 30 \times 10 = 30,000 \text{ ft}^3 = 850 \text{ m}^3$, $A = 2 \times 100 \times 10 + 2 \times 30 \times 10 + 100 \times 30 = 2,000 + 600 + 3,000 = 5,600 \text{ ft}^2 = 521 \text{ m}^2$. From Eq.4, $F = 0.25 \times 850/521 = 0.41 \mu g/h/m^2$.

Due to the unusually large amount of flyash bricks used indoors for this building, and due to the use of Eq. 4 which is based on the safe value of C of EPA (exceeding the safety of OSHA) and the save value of air exchange as per ASHRAE, the value of $F = 0.41 \mu g/m^2/h$ calculated above is very safe. Therefore, in our assessment of the safety of mercury vapor emission from indoor flyash bricks, we shall use the simple and safe threshold level of $F = 0.4 \mu g/h/m^2 = 400 \text{ Ng/h/m}^2$. Any group of flyash bricks that has a value of F less than $0.4 \mu g/h/m^2$ (or less than 400 Ng/h/m^2), as determined from a correct experimental procedure, will be considered “very safe”.

3. EXPERIMENT

3.1. Experimental Setup

Laboratory experiments were planned to measure the mercury vapor flux, F , emitted from flyash bricks, to see whether the value of F measured is below the threshold level of $0.4 \mu g/h/m^2$ determined above. If the measured value is below the threshold value, then the mercury emission rate from the flyash bricks is considered safe and vice versa.

The experimental apparatus (test system), as shown in Figure 1, consists of the following key components: (1) an environmental chamber (also called “**E-chamber**” or “**dynamic flux chamber**”) that encloses the bricks to be tested, (2) the test bricks, (3) a main Hopcalite (H1) filter for measuring the amount of mercury in the air passed through the filter, (4) a second Hopcalite filter (H2) to measure the amount of mercury leaked through the main filter H1, (5) a vacuum pump (P1) that pumps the air through the environmental chamber and through the Hopcalite filters, (6) a flowmeter (F1) to measure the volumetric flowrate (discharge) pumped through the filters, (7) a manometer (M1) to measure the negative gage pressure (vacuum) of the air inside the environmental chamber, (8) three cock valves to control the flow on-off (V1, V2 and V3), and (9) connecting tubings (T1).

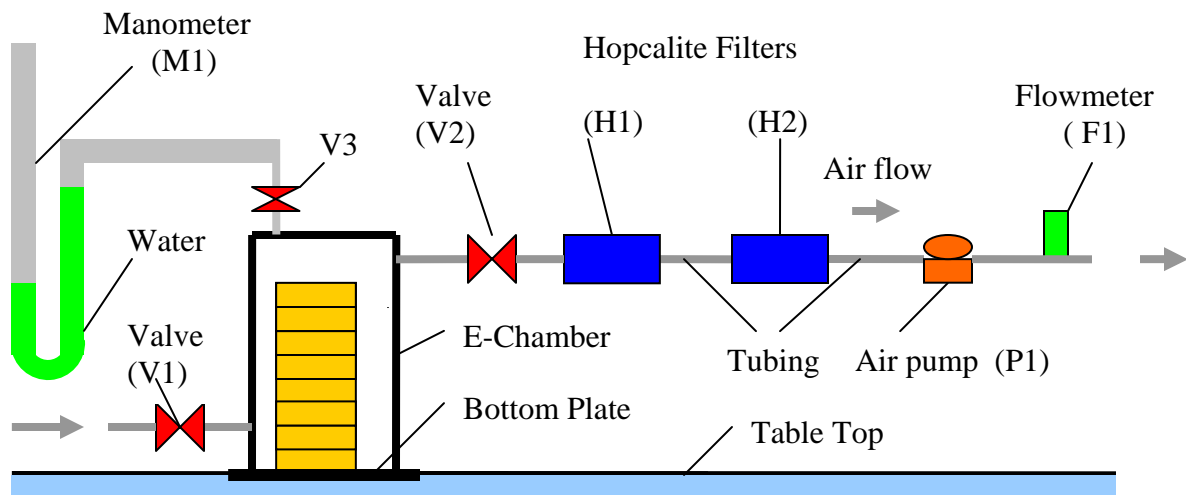


Figure 1 Experimental system for measuring mercury vapor emission from flyash bricks

The E-chamber is a useful scientific method to determine the emission of pollutants such as mercury from soil or other materials [5]. The E-chamber used in the present flyash brick study is a box of 24" (height) x 24" (length) x 12" (width) approximately, made of transparent polycarbonate plates of $\frac{1}{4}$ " (6.4 mm) thickness. The internal volume of the chamber is approximately 3.76 ft^3 (0.107 m^3); it can enclose 40 bricks of 8" (length) x 4" (width) x 2" (depth) each, stacked in 5 adjoining columns each of which with 8 bricks in each column – see Figure 1. The total internal surface area of the chamber is approximately 15.3 ft^2 (1.42 m^2); the total external surface area of the stacked-brick wall in the chamber is approximately 7.38 ft^2 or 0.686 m^2 . Polycarbonate plates instead of Plexiglas plates were used to maximize the strength of the chamber and minimize the adsorption of mercury and other pollutants. The chamber is made of two separate pieces – an open-bottom box that consists of the top (ceiling) and 4 walls, and the bottom plate. Once bricks are placed onto the bottom plate, the open-bottom box is then placed on the bottom plate to enclose the bricks as shown in Figure 1. Then the two parts of the chamber are tied together by two straps, and the contact surface between the two parts (i.e., the bottom edge of the chamber) is sealed with rope caulk. The chamber has three taps made of $\frac{1}{4}$ " (6.4 mm) I.D. polycarbonate tube – one on the top and two on opposite walls of the chamber. While the top tap is for connection to the manometer, the two end taps are for inflow/outflow to/from the chamber.

Two identical Hopcalite filters (SKC Anasorb C300, Type B), H1 and H2 as shown in Figure 1, were used to adsorb the mercury vapor in the air going through the filter. The two were connected in series so that the leakage rate of the filters can be determined in the manner described in Appendix 1. The use of the two filters insures accurate determination of the amount of the mercury in the incoming air. As explained in the Appendix, use of double filters (i.e., two filters in series) is necessary when the filter efficiency is low, as it is in this case.

The same system as shown in Figure 1 was also used to measure the mercury in air coming from an empty chamber (i.e., chamber without bricks), and to measure the mercury in the ambient air (i.e., the room air outside the E-chamber). The empty chamber measurement gives the background emission of mercury from the empty chamber, and the ambient air measurement gives the mercury in the ambient air.

The air pump, P1 in Figure 1, is a compact air compressor (Rietschle Thomas Model LGH-106, Type SP, 1/12 HP) bought from McMaster-Carr. The pump can be used either as a compressor or vacuum pump, depending on how it is installed in the system. The way that it is installed in the system as shown in Figure 1, it works as a vacuum pump to create a vacuum in the E-chamber. It is important to create a vacuum instead of positive pressure inside the E-chamber in order to maximize the release of mercury vapor from the bricks in the chamber. Note that the flux of mercury and other pollutants released from bricks and other objects depends on the air pressure around the bricks or object – increasing flux with decreasing air pressure. Because the air pressure inside a house is normally atmospheric or zero gage pressure, except during strong winds when the indoor air pressure can be negative or slightly vacuum [6], it is not conservative to run tests with the pressure in the air chamber to be positive or above atmospheric. Creating a vacuum as it is done in this experiment is more conservative in determining the safety of indoor release of mercury from bricks.

The flowmeter, F1, used in this study is DryCal DC-Lite, which is based on the principle of *prover* [7]. During measurements, the flow through the flowmeter is diverted to a prover which is a vertical glass tube in which a graphite-composite piston moves with the upward airflow. The time measured for moving the piston a given distance (from the bottom of the tube to the top of the tube) is used to calculate the flow rate, which is displaced in digital form on the screen of the flowmeter. Each measurement of the flow rate takes only a few seconds. When measurements are not taken, the airflow goes through the bypass line unimpeded.

The manometer, M1, is used to monitor the vacuum in the E-chamber. The manometer is a simple U-tube with one end open to the atmosphere, and the other end connected to the E-chamber, as shown in Figure 1. The manometer fluid is distilled water mixed with a small amount of green fluorescent dye and a surfactant (wetting agent) to decrease capillary effect due to surface tension.

The cock valves, V1 and V2 in Figure 1, are for control of the flow (both on-off and throttling). The valves are both **on** when air is being pumped through the system, and **off** when the system is not being tested. They are used to throttle the flow when adjusting the flow rate and the vacuum in the E-chamber. V3 is another cock valve in the line connecting the environmental chamber to the manometer. It is open only when reading the manometer; it is closed during ordinary operation so that the vapor of the fluorescent dye and the water vapor generated by the manometer fluid will not diffuse into the E-chamber to contaminate the air in it.

The tubing connecting the various parts of the system is Tygon tubing of ¼" (6.4 mm) I.D. It also fits the two ends of the Hopcalite filters.

3.2. Test Materials (Flyash and Bricks Used)

The first set of 40 bricks used in the tests, each measuring 8" (length) x 4" (width) x 2" (depth), were made of high-grade (low "Loss-on-Ignition" or LOI) flyash from the Thomas Hill Power Plant in Missouri. The bricks were compacted at 1,800 psi, using a mixture that has a flyash to water ratio equal to 7.4, and an air-entrainment agent of 0.2%. The bricks were steam-cured at 150° F for 24 hours, followed by air cure (allowing them to dry naturally in a room) for approximately 60 days. The fly ash that was used in making the bricks had a mercury concentration of less than 0.1 µg/g, which is the same as 0.1 wppm (weight parts per million).

3.3. Test Condition

The tests were carried out in a ventilated room in the Freight Pipeline Company building. The tests were conducted in winter (January 15 –March 8, 2007). The building temperature was automatically controlled by a thermostat system, with temperature varying from 53 °F (12 °C) after work and during weekends, and 73 °F (23 °C) during working hours. No attempt was made to conduct the tests outside this temperature range. No attempt was made either to control or record the barometric pressure inside the room.

3.4. Test Procedure

For each set of the flyash bricks, the test procedure consists of three major steps (three separate test runs): (A). Test of mercury in the air passing through the E-chamber with 40 bricks; (B) test of mercury in the air passing through the empty E-chamber without bricks; (C) test of mercury in the ambient air. Each of the three major steps consists of several sub-steps as follows:

(A) Test Air through E-Chamber with Bricks:

1. Set up the test system as shown in Figure 1, with two Hopcalite filters H1 and H2 connected in series, and with 40 bricks in the chamber.
2. Seal the contact between the bottom of the E-chamber and the bottom plate with rope caulk to minimize air leakage through the contact.
3. Open the 3 valves V1, V2 and V3 before turning on the pump⁴. Then, turn on the pump and measure the manometer reading ΔH which is the differential height of the water in the two legs of the manometer. Record the ΔH and the time when the manometer reading is taken. (Note: Make sure that the cap on the top of the right leg of the manometer is open or loose so that atmospheric pressure exists at one end of the manometer. Otherwise, erroneous manometer reading would occur.)
4. As soon as the manometer reading is taken, close valve V3, the valve connected to the manometer.
5. Pump air through the system for at least 24 hours. Measure the flow rate (discharge) Q through the system in the beginning, at the end, and at least five times each day during the experiment. The duration of the experiment is T given in minutes (e.g., 24 hrs is recorded as 1,440 minutes.)

⁴ Having the valves closed when the pump is on may damage the pump.

6. Stop the pump, remove (disconnect) the two Hopcalite filters from the system, cap their two ends, and label each filter.
7. Place the capped filters in a plastic zip-lock bag for temporary storage in a refrigerator. After the other two steps (B) and (C) are also completed, all the samples (filters) are sent to an outside chemical lab for analysis of the amount of mercury adsorbed on each filter.
8. From individual readings of the discharge (volumetric flow rate) of air pumped through the system, Q , and from the corresponding time t at which each Q was measured, the temporal mean value of discharge, Q_o , can be determined from numerical integration by using an Excel spread sheet. The total volume of air that has passed through the filters during the test is then:

$$V_F = TQ_o \dots\dots\dots (5)$$

For instance, if T is 24 hours (1440 minutes) and Q_o is 2.11 L/min (liter per minute), from Eq. 5, $V_F = 1440 \times 2.11 = 2405 \text{ L} = 84.9 \text{ ft}^3 = 2.40 \text{ m}^3$.
 (Note: $1 \text{ ft}^3 = 28.3 \text{ L}$, and $1 \text{ m}^3 = 35.3 \text{ ft}^3 = 1,000 \text{ L}$.)

9. Use Eq.5 and the other equations derived in Appendix 1 to calculate the filter efficiency E_1 and the mercury concentration in the incoming air, C_a .

(B) Test Empty E-Chamber:

1. Use the system as shown in Figure 1 except that no bricks are placed inside the E-chamber.
2. Use the same test procedure (steps 1 through 9) as in (A) above.

(C) Test Ambient Air:

1. Use the same system as in (A) and (B), except that no E-chamber is used. The ambient air in the same room where the E-chamber is located is pumped through the two Hopcalite filters and the flow meter.
2. Use the same test procedure as described in (A).

4. TEST RESULTS

So far, only two sets of tests were conducted with bricks made from flyash of the Thomas Hill Power Plant in north central Missouri. They are: Set 1- Preliminary Tests, and Set 2- Improved Tests. Runs 1 through 6 belong to Set 1, whereas Runs 10 through 12 are for Set 2. Set 2 are improved from set 1 in that each run of the Set was conducted over a longer period of time (7 days instead of 2 days in Set 1), thereby having more mercury accumulated on each filter and making measurements of mercury more accurate. Also, as part of Set 2, the background level of mercury on three blank Hopcalite filters was determined, which is more accurate than the average value supplied by equipment manufacturer used in Set 1. While the equipment manufacturer gave the average value of 50 Ng mercury on each 500 mg Hopcalite filter [8], the chemical laboratory that did analysis for us (Company A mentioned in the next paragraph) found that the three blank filters contained 83, 84 and 86 Ng per filter [9]. The average or mean of the three is 84.3 Ng, which is the value used in our analysis.

This mean value was subtracted from the value measured by each test filter to determine the amount of mercury adsorbed by the filter from air during the test.

4.1. Set 1 (Preliminary Test) Results

The result of Set 1 tests is summarized in Table 1. All the six runs listed in this table were conducted under similar conditions. Note that each column of the table is numbered and marked on the bottom of the column heading. Column 1 gives the run numbers. Columns 2 through 5 give respectively the measured average flow rate Q, the test period T, the air flow volume V during the test period, and the amount of vacuum in the E-chamber (in inches of water).

Table 1 Mercury emission from flyash bricks (Set 1: Preliminary Test)

Run No.	Aver. Air Flow Rate, Q (L/min)	Test Period T (hrs)	Air Flow Vol., V (m ³)	Vacuum In Inches of Water (inch)	Mercury on Filter (Ng)			Captured Mercury Concen. C ₂ (Ng/m ³)	Filter Efficiency, E ₁ (%)	Total Mercury Concen. C _m (Ng/m ³)	Mercury Flux, F (Ng/h/m ²)	Test Condition
					H1	H2	H1+H2					
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
1	2.77	24.8	4.12	16	95 (10.7)	91 (6.7)	186 (17.3)	4.20	37.4	6.95	-0.343	Empty Chamber
2	3.23	48.0	9.30	15	<250 (<166)	<250 (<166)	<500 (<332)	<35.7	37.4	<47.7	<0.34	Empty Chamber
3	3.39	48.5	9.86	14	86 (1.67)	110 (25.7)	196 (27.3)	2.77	37.4	0.461	-1.92	40 Bricks
4	3.86	48.2	11.2	14	<250 (<166)	<250 (<166)	<500 (<332)	<29.6	37.4	<39.6	<-2.73	40 Bricks
5	3.83	48.9	11.2	0	--	--	210 (41.3)	3.69	37.4	9.88	--	Ambient
6	3.13	52.3	9.82	0	<250 (<166)	--	<500 (<332)	<33.8	37.4	<45.2	--	Ambient

Note: The filters of Runs 1, 3 and 5 were chemically analyzed by Company A, and the filters of Runs 2, 4 and 6 were chemically analyzed by Company B. Negative values of F represents adsorption instead of emission of mercury vapor.

The amount of mercury measured on each test filter, H1 and H2, is given in columns 6 and 7, with the sum of the two given in column 8. For comparison purpose, test filters were sent to two different companies, A and B, for analysis. Company A was asked to analyze the filters of Runs 1, 3 and 5, whereas Company B was asked to analyze the filters of Runs 2, 4 and 6. It turned out that Company A could measure the weight of mercury on filters down to 1 Ng, whereas Company B could not measure anything less than 250 Ng. Since all the test results were less than 250 Ng, Company A was selected for subsequent measurements, and no more samples were sent to Company B for measurement. Company A is a local company (Laboratory & Environmental Testing, Inc.).

In columns 6 through 8, test values as reported by the chemical labs are listed first, with the corrected values listed in parentheses below them. The correct values are the test values minus the background values on each filter. The background values were assumed to be the mean of the three tested blank Hopcalite filters, namely, 84.3 Ng. It can be seen from the values listed in these three columns that the corrected values are much smaller than the uncorrected values, showing that the test period of 2 days must be increased in order to get larger corrected values, and to get better overall accuracy.

In spite of the inaccuracy of the Set 1 tests, the data still show a general trend and hence were useful and analyzed. For instance, Run 1 showed that the first Hopcalite filter captured 10.7 Ng of mercury, whereas the second filter captured only 6.7 Ng of mercury. Using equations derived in Appendix 1, it was possible to use these values to determine the filter efficiency, which turned out to be only 37%, approximately. The values of mercury listed in columns 6 through 8, for runs 2, 4, and 6, are those measured by Company B. As can be seen from the table, these values are all within 250 Ng for single filters, and within 500 Ng for two filters. They are correct but of not much value. Far more meaningful information can be obtained from the more accurate measurements taken by Company A.

A questionable data in Table 1 is the mercury measured for Run 3. The test results showed that the first filter, H1, adsorbed only 1.67 Ng whereas the second filter, H2, adsorbed 25.7 Ng. The result is unexpected and questionable because we expect the first filter to adsorb more than the second filter. This questionable result raises the following possibilities: (1) There may be a human error in labeling or handling the samples, causing a switch of the two values, (2) the two Hapcolite filters used in the test may have very different characteristics including background level of mercury (this is a less likely possibility), and (3) the first filter being located upstream of the second filter may have lost some of the Hopcalite powder, which ended up in the second filter downstream. The aforementioned three possibilities have little effect on the sum of mercury accumulated on the two filters, which is believed to be reliable. It is for this reason that the analysis of the data for Run 3 was based the sum H1 plus H2, rather than the two individual values H1 and H2.

Column 8 gives the sum of the values on the two filters, H1 and H2, connected in series as shown in Figure 1. Column 9 gives the concentration of mercury in the air captured by both filters, assuming that the two filters working together can capture 100% of the mercury from the entering air. This means that the values in column 9 are obtained by dividing the values of column 8 by the air volume in column 4. This yields an approximate value of the mercury in the incoming air.

In Table 1, the filter efficiency of the two filters used in Run 1 was calculated from Eq.A-9, yielding a value of 37.4% (see Example 2 in Appendix 1). Then it was assumed that all the other filters used in Set 1 had the same filter efficiency (see column 10). This is not strictly correct but approximately correct. By using this assumption, Eq.A-7 was used to calculate the approximate mercury concentration in the incoming air, C_m , with results given in column 11. Note that

both C_2 in column 9 and C_m in column 11 represent the mercury concentration of the incoming air. Due to different assumptions used for calculating C_2 and C_m , their corresponding values are significantly different as shown in Table 1. However, to be conservative or on the safe side in this study, the larger of the two values for each case will be used in interpreting the results, and in calculating the flux values, F , given in column 12. This explains how the various values in Table 1 were obtained.

4.2. Set 2 (Improved Test) Results

Due to the unacceptable errors of the initial test (Set 1), a second (improved) set of experiments were run to obtain more reliable test results. The results are given in Table 2. The three test runs of Set 2 are: Run 10 for test with 40 bricks in the E-chamber, Run 11 for testing of the ambient air, and Run 12 for testing the empty chamber. In each run, the test was conducted uninterrupted for 7 to 8 days. As can be shown from the values in Columns 6 through 8, in general more mercury was reported on measured filters than in the initial test. The only exception is for H2 of Run 10, which reported a mercury level 52 Ng which is 32.3 Ng less than the average background level on the filter. This happened only for Run 10, which is the case with 40 bricks in the E-chamber. A plausible explanation of this data is that since the air coming out the E-chamber has been scrubbed of its mercury by the fly ash bricks, the air after having passed through the first filter became very pure. This pure air passing through the second Hopcolite filter (H2) that contains an average of 84.3 Ng of mercury is washing out the Hg from the second filter, similar to the behavior of sand filters for water supply during the backwash stage. (Note: The use of sand filter as an analogy is not to be misunderstood. The two types of filters are based on different principles: while sand filters are based on physical filtering, the Hopcalite filters are based on chemical adsorption. However, the two types of filters based on quite different principles can have similar behavior.)

Table 2 Mercury emission from flyash bricks (Set 2: Improved Test)

Run No, (1)	Aver. Air Flow Rate, Q (L/min) (2)	Test Period T (hrs) (3)	Air Flow Vol., V (m ³) (4)	Vacuum (inch H ₂ O) (5)	Mercury on Filter (Ng)			Captured Mercury Concen. C ₂ (Ng/m ³) (9)	Filter Efficiency, E (%) (10)	C _m (Ng/m ³) (11)	Hg Flux, F (Ng/h/m ²) (12)	Test Condition (13)
					H1 (6)	H2 (7)	H1+H2 (8)					
10	4.12	191.6	47.4	2.3-4.9	110 (25.7)	52 (-32.3)	162 (-6.7)	-0.141	100	0.542	-0.081	40 Bricks
11	4.00	167.5	41.2	0	120 (35.7)	98 (13.7)	218 (49.3)	1.20	61.6	1.41	--	Ambient Air
12	4.25	169.0	43.1	1.4 – 1.6	110 (25.7)	90 (5.7)	200 (31.3)	0.726	77.8	0.766	-0.12	Empty Chamber

Table 2 shows that from the improved tests, the filter efficiency (see column 10) ranges from 62% to 100%. This appears to contradict the finding in [10], which found the Hopcalite filter efficiency to be higher than 92%. However, this apparent contradiction can be explained. The minimum concentration of mercury used in the tests of [10] was 0.026 mg/m^3 or $26,000 \text{ Ng/m}^3$, whereas the mercury concentration in the air, C_m , measured in our experiment is less than 10 Ng/m^3 . The former is more than a thousand times higher in concentration than the latter. It is quite possible that at very low concentration of mercury in air (about 3,000 times less than that used in the tests of [10]), the filter efficiency is significantly less than 100%. This shows the necessity of using two identical filters in series, as we have analyzed theoretically in Appendix 1, to determine the filter efficiency and the correct amount of mercury measured in the incoming air, when the concentration of mercury in the air is very low. As explained before, the filter efficiency E_1 is determined from Eq.A-9, whereas the mercury concentration in the incoming air, C_m , is determined from Eq.A-7.

In Table 2, the value of C_m (concentration of Hg in the air samples taken) is the largest for the ambient air (1.41 Ng/m^3), the second largest for the empty E-chamber (i.e., chamber without bricks) (0.766 Ng/m^3), and the smallest for the chamber filled with 40 fly ash bricks (0.542 Ng/m^3). ***This shows that the chamber and the bricks not only do not emit mercury vapor, they actually adsorb mercury vapor contained in the ambient air.*** The bricks are especially effective in absorbing mercury. They absorb mercury at a flux rate of 0.081 Ng/h/m^2 , approximately. This seems to suggest that the flyash bricks may have value in reducing mercury in indoor air.

Another piece of evidence that supports the conclusion that flyash bricks help to clean up indoor air is the value of 1.41 Ng/m^3 measured for our ambient air. In this case, the ambient air is the room air where the tests were conducted. According to a recent study [11], which measured both the indoor and outdoor air in two New Jersey cities, the mean value of the mercury measured outdoors was about 5 Ng/m^3 , whereas the mean value of mercury measured indoors in residential buildings was about 25 Ng/m^3 . This shows that the mercury concentration in the indoor air where our experiments were conducted is 17 times lower than the mean indoor level of mercury measured in the New Jersey buildings. While comparing the levels between two different communities raises other contributing factors, a possible contributing factor for the relatively clean indoor air in our laboratory is that there were many flyash bricks stored nearby, which adsorb mercury from the indoor air.

One may wonder why the flyash bricks adsorb mercury from instead of release mercury to the ambient air, and whether such findings are believable. It should be pointed out that in a 2003 paper presented to the International Ash Utilization Symposium [12], Hassett and Heebink stated the following: ***“The results of the recently completed blank determination have confirmed what had been previously suspected: the CCBs selected for this research were acting, for the most part, as mercury sinks rather than as mercury sources.”*** If such behavior happens to CCBs (coal combustion byproducts) including fly ash, why cannot the same also hold for products such as bricks

made from flyash? The current study provided the first evidence that bricks made from 100% flyash also behave as a sink rather than source of mercury. This is good news for flyash bricks since they will be used in the future both indoors and outdoors. When used indoors the flyash bricks are expected to clean up the indoor air (for mercury at least if not also for other pollutants) instead of polluting the air, making the indoor air cleaner than the outdoor air in the environment.

5. CONCLUSION

Based on both the preliminary tests (Set 1), and the improved tests (set 2), it can be concluded that ***the flyash brick not only does not release mercury contained in the brick into the environment, it actually adsorbs mercury from the ambient air. This means that the use of flyash bricks indoors will benefit rather than harm the indoor air quality.*** More tests will be conducted in the future to further verify the conclusions reached in this study. The future tests will use a much longer duration for each test than used in the current tests (about one month), so that even more accurate test data can be obtained.

6. ACKNOWLEDGMENT

Sponsorship of this research by the National Science Foundation (NSF) under the Small Business Innovation Research (SBIR) Phase II Program (NSF Grant No. 0548719) is much appreciated!

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Appendix 1: Filter Efficiency Test and Analysis

When using special filters such as the Hopcalite filters of the SKC Inc. to measure mercury vapor in air, it is important that the filters capture most of the mercury vapor contained in the air passing through the filter. To insure that this is the case when the mercury concentration in the air is very low as in this study, a filter efficiency test needs to be conducted. This can be done as follows:

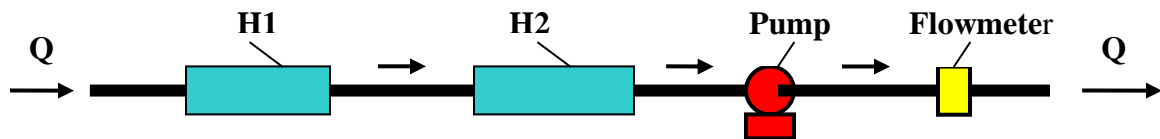


Figure 2 Filter efficiency test

Connect two identical Hopcalite filters, H1 and H2, in series as shown in Figure 2. The air is pumped from left to right through both filters at a steady rate (volumetric flow rate) of Q (m^3/s). Assume that the incoming air contains C_m micrograms of mercury per cubic meter of air ($\mu\text{g}/\text{m}^3$), assume each filter

contains x micrograms (μg) of background level of mercury (i.e., the level of mercury that exists in each filter before the filter was used). If the flow is continued at the steady rate Q over a period of T (in seconds), and if at the end of the period T the mercury measured (accumulated) on the two filters H1 and H2 are respectively M_1 and M_2 in micrograms, from mass balance we have the following:

The amount of mercury in the air entering the system in time T is:

$$M_0 = QC_m T \quad \dots\dots\dots (A-1)$$

The amount of mercury adsorbed on filter F1 in time T is:

$$M_1 = QC_m T E_1 \quad \dots\dots\dots (A-2)$$

where E_1 is the efficiency of filter F1 in absorbing mercury vapor.

The amount of mercury in the air leaked through filter F1 in time T is:

$$M_{1L} = QC_m T (1-E_1) \quad \dots\dots\dots (A-3)$$

The amount of mercury absorbed on filter H2 in time T is:

$$M_2 = QC_m T (1-E_1) E_2 \quad \dots\dots\dots (A-4)$$

where E_2 is the efficiency of filter H2 in absorbing mercury vapor.

Assuming that filter H1 and H2 contain background levels of mercury of M_{1B} and M_{2B} respectively. Then, from Eq. A-2, the total amount of mercury measured on filter 1 from the flow test is:

$$M_{1T} = M_{1B} + M_1 = M_{1B} + QC_m T E_1 \quad \dots\dots\dots (A-5)$$

Likewise, the total amount of mercury measured on filter 2 from the flow test is:

$$M_{2T} = M_{2B} + M_2 = M_{2B} + QC_m T (1-E_1) E_2 \quad \dots\dots\dots (A-6)$$

Finally, from Eq.A-5, the efficiency of the first filter (H1) can be calculated from

$$E_1 = \frac{M_{1T} - M_{1B}}{QC_m T} \quad \text{or} \quad C_m = \frac{M_{1T} - M_{1B}}{QE_1 T} \quad \dots\dots\dots (A-7)$$

From Eq.A-6, the efficiency of the second filter (H2) is

$$E_2 = \frac{M_{2T} - M_{2B}}{QC_m T (1-E_1)} \quad \text{or} \quad C_m = \frac{M_{2T} - M_{2B}}{QE_2 T (1-E_1)} \quad \dots\dots\dots (A-8)$$

Equations A-7 and A-8 can be used to determine the filter efficiency from the flow test, for both filter H1 and H2, provided that the mercury concentration in the

incoming air, C_m , is known. Conversely, if the filter efficiency E_1 is known, the concentration of mercury in the incoming air, C_m , can be determined from Eq.A-7.

If identical filters are used for the test, E_1 and E_2 have the same value. In such a case, combination of Eqs. A-7 and A-8 yields:

$$E_1 = E_2 = \frac{M_{1T} - M_{1B}}{QC_m T} = \frac{M_{2T} - M_{2B}}{QC_m T(1 - E_1)},$$

which yields:

$$1 - E_1 = \frac{M_{2T} - M_{2B}}{M_{1T} - M_{1B}}, \text{ or } E_1 = 1 - \frac{M_{2T} - M_{2B}}{M_{1T} - M_{1B}} \dots\dots (A-9)$$

From Eq. A-9, the filter efficiency E_1 (same as E_2), can be calculated from the test values of M_{1T} , M_{1B} , M_{2T} and M_{2B} .

Assuming that the two filters H1 and H2 are identical, $M_{2B} = M_{1B}$. From Eq.A-9, E_1 can be determined accurately only if the value of M_{1T} is much larger than the value of M_{1B} , and if M_{2T} is larger than or equal to M_{2B} but much smaller than M_{1T} .

The foregoing derivation is rather general. If the incoming air is drawn directly from the ambient air, the mercury concentration C_m is then that of the ambient air, namely, $C_m = C_a$. On the other hand, if the incoming air is drawn from the E-chamber containing bricks as shown in Fig. 1, then $C_m = C_b$. Finally, if the incoming air is drawn from the E-chamber when it is empty (without bricks), $C_m = C_e$.

Suppose that the system in Fig.2 is used in separate tests of ambient air, empty chamber and chamber with bricks. From the test values, Eq.A-7 can be used to determine the mercury concentration of the ambient air, C_a , the mercury concentration of the air through the empty chamber, C_e , and the mercury concentration of the air through the chamber with bricks, C_b . Under steady state condition, the rate of emission of mercury by the empty chamber is:

$$R_e = Q(C_e - C_a) \dots\dots\dots (A10)$$

And, the emission flux of the empty chamber becomes

$$F_e = \frac{R_e}{A_e} = \frac{Q(C_e - C_a)}{A_e} \dots\dots\dots (A11)$$

where A_e is the internal surface area of the empty chamber.

Likewise, under steady state, the rate of emission of mercury by the bricks in the chamber is

$$R_b = Q(C_b - C_e) \dots\dots\dots (A12)$$

$$F_b = \frac{R_b}{A_b} = \frac{Q(C_b - C_e)}{A_b} \dots\dots\dots (A13)$$

where A_b is the surface area of the brick wall in Fig. 1, in contact with air.

The foregoing equations can be used to calculate the key values of this study, as shown in the following example:

Example 2. Suppose that the Hopcalite filters that we use have a value of M_{1B} and M_{2B} of 84.3 Ng per filter (average value of 3 blank filters measured by LET Laboratory). From the above, for accurate measurement we must make M_{1T} much larger than 84.3 Ng. Since from Eq.A-5 $M_{1T} = M_1 + M_{1B} = M_1 + 84.3$, this means we must make M_1 much larger than 84.3 Ng.

Based on test data listed in Table 1, for Run No.1 (empty chamber) we have M_{1T} and M_{2T} equal to respectively 95 and 91 Ng. Thus, from Eq.A-9, the filter efficiency is:

$$E_1 = 1 - \frac{91 - 84.3}{95 - 84.3} = 1 - \frac{6.7}{10.7} = 1 - 0.626 = 0.374 = 37.4\%.$$

This shows a low efficiency of the filter.

For Run 1, $Q = 2.77 \text{ L/min} = 0.0000462 \text{ m}^3/\text{s}$, $T = 24.75 \text{ hrs} = 89,100 \text{ s}$, and $QT = 4.12 \text{ m}^3$. From Eq.A-7, the value of C_m can be calculated as follows:

$$C_e = C_m = \frac{M_{1T} - M_{1B}}{QTE_1} = \frac{95 - 84.3}{4.12 \times 0.374} = \frac{10.7}{1.540} = 6.95 \text{ Ng} / \text{m}^3$$

For Run 5 (ambient air measurement), $QT = 11.2 \text{ m}^3$. From Eq.A-7,

$$C_a = C_m = \frac{M_{1T} - M_{1B}}{QTE_1} = \frac{210 - 84.3 \times 2}{11.2 \times 0.374} = \frac{41.4}{4.19} = 9.88 \text{ Ng} / \text{m}^3$$

For Run 3, it is assumed that the filter efficiency is the same as for Run 1 (i.e., $E_1 = 37.4\%$ or 0.374). Thus, from Eq.A-7,

$$C_b = C_m = \frac{M_{1T} - M_{1B}}{QTE} = \frac{86 - 84.3}{9.86 \times 0.374} = \frac{1.7}{3.69} = 0.461 \text{ Ng} / \text{m}^3.$$

From Eq.A-10, the emission rate of mercury by the empty E-chamber is $R_e = Q(C_e - C_a) = 0.0000462 \text{ m}^3/\text{s} \times (6.95 - 9.88) \text{ Ng}/\text{m}^3 = -0.000135 \text{ Ng}/\text{s} = -0.487 \text{ Ng}/\text{h}$. The flux rate of emission from the E-chamber is $F_1 = R_1/A_e$, where A_e is the empty chamber internal area in contact with air, 1.42 m^2 . Thus, $F_e = -0.487/1.42 \text{ m}^2 = -0.343 \text{ Ng}/\text{h}/\text{m}^2$.

From Eq.A-13, the flux rate from the brick is $F_b = Q(C_b - C_e)/A_b = 0.203 \text{ m}^3/\text{h} \times (0.461 - 6.95) \text{ Ng}/\text{m}^3 / 0.686 \text{ m}^2 = -1.92 \text{ Ng}/\text{h}/\text{m}^2$.