FATE OF MERCURY COLLECTED FROM AIR POLLUTION CONTROL DEVICES

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INTRODUCTION

Mercury that enters a coal-fired power plant originates from the coal that is burned and leaves through the output streams, which include stack emissions and air pollution control (APC) residues (either in solid or liquid form). This article describes recent findings on the fate and environmental stability of mercury in coal combustion residues (CCRs) such as fly ash and solid products from flue gas desulfurization (FGD) scrubbers when either disposed or reused in agricultural, commercial, or engineering applications.

New environmental regulations in the U.S. will result in lower mercury air emissions, but potentially more mercury in CCRs. The Clean Air Mercury Rule (CAMR) required the electric utility sector to remove at least 70% of the mercury released from power plant stack emissions by 2018. However, CAMR was vacated by the Court in 2009. New rules are currently being worked on. Twenty states have implemented their own regulations already, according to the National Association of Clean Air Agencies.[1] Other EPA regulations will necessitate the addition of new air pollution control devices for NOx and SO_2 at some power plants. This can also affect the fate of mercury in those plants.

PATHWAYS FOR MERCURY IN COAL-FIRED POWER PLANTS

The major mercury-containing input to a power plant is coal. The average mercury content in U.S. coals is 0.1 μg/g (Table 1).[2] Practically speaking, all mercury in the fuel is converted to elemental mercury vapor during coal combustion. As the flue gas cools, some of the elemental mercury may be oxidized. Both gaseous elemental and oxidized mercury can be adsorbed on suspended particles (fly ash), which consists of inorganic ash and unburned carbon. At the inlet of the air pollution control devices (APCDs), mercury

can be found in the gaseous elemental (Hg^o), gaseous oxidized (Hg^{2+}), and particulate bound (Hg_p) forms.

Air pollution control devices designed to capture SO_2 and particulate matter (PM) can also remove mercury from flue gases in two ways: removal of Hg_p in particulate control devices and removal of Hg^{2+} in FGD scrubbers. Thus, the mercury removed from the flue gas may be found in fly ash and in the scrubber solids and liquid effluent. This approach to mercury control is popularly known as a "co-benefits" strategy.

The mercury that is removed in the FGD scrubber can partition to the solid or liquid streams. Figure 1 illustrates the measured partitioning of mercury in FGD outlet streams at five pulverized-coal fired power plants.[3] The plants fired bituminous coals and had cold-side ESPs for particulate control. Each of these plants had a selective catalytic reduction (SCR) system for NO_x control and a wet FGD using calcium-containing slurry to control SO_2. Gaseous mercury removal by the FGDs ranged from 77% to 95%, and the mercury largely ended up in the scrubber solids.

Mercury appears to be concentrated in fine particles of scrubber solids that are predominantly iron oxyhydroxides, and is not strongly associated with the solid calcium sulfate in the scrubber.[4,5] In some wet FGD systems, the fine solids are recycled back to the scrubber after dewatering of the byproduct solid, while in others, they are disposed of, as was the case for two FGDs noted in an EPRI study.[6] Table 2 shows the distribution of mercury in the scrubber outlet streams for three limestone scrubbers in the EPRI study. For the two forced-oxidation scrubbers sampled, most of the mercury leaving the scrubber did so in the gypsum fines or fines liquor after the dewatering process. In forced oxidation scrubbers, this means that mercury can ultimately be in the gypsum fines as well as in the FGD byproduct.

Dedicated mercury control technologies can be applied to plants to increase the amount of mercury removed from the flue gas. The most widely applied mercury control technology at coal-fired power plants is activated carbon injection (ACI). In the simplest

application, all the activated carbon is collected with the fly ash generated by the plant, which results in a mixture of fly ash and spent sorbent that is higher in mercury than the fly ash alone. In some instances, a new fabric filter is added after the plant's existing PM control device, so that the activated carbon that is injected into the flue gas can be collected separately from the fly ash. This approach preserves the economic value of the fly ash by keeping it separate from activated carbon. The presence of activated carbon can impair one of the key uses of fly ash as a replacement of Portland cement in concrete (i.e., 14.5 million tons in 2007 or 26% of total amount of CCRs re-used). Concrete-friendly activated carbons have been developed to alleviate this problem.

COAL COMBUSTION RESIDUES

According to the American Coal Ash Association[7], approximately 40% (51 out of 126 million tons) of all CCRs produced in the United States are used in commercial or engineering applications to avoid land disposal. Figure 2 presents a summary of the primary uses by CCR type (e.g., fly ash, FGD gypsum, bottom ash). Of the 72 million tons of fly ash produced in 2007, 44% (32 million tons) was used in commercial applications such as making cement-related products, structural fill, and highway construction. Eight million tons of the FGD gypsum that was produced (or ~70%) was used in making wallboard. Figure 3 illustrates the wide range of mercury concentrations that have been found in fly ash (527 ng/g average, 16 to 1530 ng/g range) and FGD gypsum (512 ng/g average; 9 to 1110 ng/g range).[8,9,10]

STABILITY OF MERCURY IN COAL COMBUSTION RESIDUES

Leaching Behavior of Mercury in CCRs

When there is no beneficial use for fly ash or FGD solids, they are often placed in landfills or ponds, where mercury (and other trace metals) might be leached out. Historically, single-point pH leaching tests have been used to support CCR management decisions. The U.S. EPA's Science Advisory Board[8] and the National Academy of Sciences[11] raised concerns over the use of single-point pH tests that do not reflect the actual conditions under which CCRs are typically managed. Because metal leaching

rates change with changing environmental conditions (especially pH), the concern is that the existing leach tests being used for CCR management decisions may not be the most accurate predictor of potential environmental release of mercury or other metals.
In response to these concerns, the U.S. EPA is using a more comprehensive leach testing framework[12,13] to investigate the potential for leaching of mercury and other metals from CCRs over the range of field conditions to which CCRs are typically exposed to during land disposal and in engineering and commercial applications. The framework includes different test methods that consider: (i) pH and LS (liquid-to-solid ratio) dependent leaching, (ii) percolation-based release using column testing, and (iii) diffusion-limited release from monoliths and compacted granular materials that behave as monoliths after placement. Public release of the draft methods is planned for fall 2009 as SW-846 Draft Methods[*].

Using the pH-LS test method, CCRs are being collected from U.S. coal-fired power plants to span the range of coal types and APC configurations. In the first report released from this EPA research, fly ashes from six facilities with and without the use of sorbents for enhanced mercury capture were evaluated.[8] Table 3 provides results for mercury, arsenic, and selenium. The results show that mercury is strongly retained by the fly ash and unlikely to be leached at levels of environmental concern. However, there is potential concern for increased mobility of arsenic and selenium. A second report provides data for a wider range of metals from evaluation of twenty-three samples collected from eight facilities that use wet FGD scrubbers.[9] Results for fly ash and FGD gypsum indicate that although there may not be a concern for leaching of mercury, other metals may be of concern (Tables 4 and 5).[9] Results also suggest that there may be more of a concern in terms of potential leaching of metals for fly ash and scrubber sludge than for FGD gypsum. The blocks that are highlighted in Tables 4 and 5 indicate where there may be potential concern when comparing the leach results to health based levels (i.e., MCL or TC). The use of these results are intended as inputs to groundwater

[*] SW846 are EPA's official compendium of analytical and sampling methods that have been evaluated and approved for use evaluating solid waste (http://www.epa.gov/osw/hazard/testmethods/sw846/index.htm).

transport and fate models which take into account attenuation and other factors important in determining levels of potential concern to human health and the environment.

Figure 4 presents mercury leach testing results across the pH range for fly ash and scrubber sludge with and without the use of post-combustion NO_x control. There appears to be an effect on the leaching behavior with the use of post-combustion NO_x control. Additional information on the fate of mercury and other metals at plants using more stringent APCDs will be reported from EPA research program as part of the work outlined in the EPA Mercury Road Map.[14] A third report is being drafted from analysis of forty-three samples obtained from sixteen facilities with multi-pollutant controls in use at coal-fired power plants. This report is expected to be released by spring 2010. A leaching assessment tool is being developed to provide easier access to the improved leach data for a range of CCRs and potential field conditions. The tool can also be used for data storage and viewing when using the new SW-846 leach test methods. The results from the leaching assessment tool are to provide more realistic leach data as input to future risk assessments and to help ensure protection of human health and the environment for future CCR management decisions.

Thermal Stability of CCRs

Some uses of CCRs may involve high-temperature processing that may increase the potential for release of mercury and other metals. In cement manufacturing, for example, CCRs may be raw feed for producing clinker in cement kilns. Virtually all mercury will be volatilized when CCRs are used as feedstock to cement kilns as the result of high operating temperatures (1450^{o}C).[15] EPA has proposed (74 FR 21136m May 6, 2009) to reduce mercury emissions from cement kilns, which may result in the use of APCDs similar to those used at coal-fired power plants (e.g., wet scrubbers and sorbents for enhanced mercury capture). The addition of APCDs at cement kilns should not affect the ability to use fly ash or FGD gypsum in the production of clinker. However, to avoid installation of APCDs, kiln inputs (such as fly ash) containing mercury may be avoided, which could impact usage of some CCRs.

There has also been concern raised for other processes, such as the production of asphalt. Using thirteen different CCRs, a laboratory simulation was conducted on asphalt production at 170 ^{o}C. The results suggest that volatilization of mercury is less than 10% except for one CCR where results suggested volatilization of 92 to 100%.[15]

The best data available for thermal stability during wallboard production are from a study of five wallboard plants where a mercury mass balance was attempted.[10] Mercury loss was evaluated for surface drying, calciners, and board-line dryers. The wide variation in mercury loss (2 to 55%) from seven FGD gypsum samples was attributed to the different conditions under which each gypsum sample was generated. This variability included coal type, APC configuration, and purge rate of fine gypsum particles.

Any remaining mercury in the finished FGD-wallboard could be released during use or subsequent disposal or recycling of the wallboard. Research is underway at EPA to evaluate the fate of mercury and other metals through each stage of the life cycle for FGD gypsum.

Curing of concrete can also involve elevated temperatures (80 ^{o}C). For a laboratory simulation experiment, mercury emissions were measured at 0.4 to 5.8 ng of mercury/kg of concrete for steam curing. The study reported Hg flux from exposed concrete surfaces to not exceed mercury fluxes from soils (4.2 ng $m^{-2}h^{-1}$). The study concluded that less than 0.022% of the total quantity of Hg present in concrete was released during the curing process. Therefore greater than 99% of the Hg was retained in the concrete under the conditions tested.[16]

Release of Gaseous Mercury from Landfills

There has been concern about the stability of mercury in fly ash or FGD waste when these materials are disposed in a landfill. Laboratory studies and field measurements of solid-gas exchange between fly ash and fly ash mixed with FGD solid mixtures have been conducted.[17] These studies have shown that fly ashes from bituminous and subbituminous coals act as a sink for atmospheric mercury, while lignitic fly ash may

emit mercury to the atmosphere. In the field, mercury fluxes (solid to gas) from both uncovered and vegetated, topsoil-covered landfills containing bituminous or mixed subbituminous-bituminous fly ash were determined to be lower than the mercury fluxes from the surrounding soils. Mercury fluxes from a landfill containing FGD solids mixed with lignitic fly ash were estimated to be about four times higher than the surrounding soil. [17]

SUMMARY

The addition of FGD systems, SCR, ACI to capture mercury, SO_2, and other pollutants will shift mercury from the stack gas to fly ash, FGD gypsum and other air pollution control residues. This may have a significant impact on fly ash production and quality. For several commercial uses, it appears less likely that mercury in CCRs will be reintroduced into the environment, at least during the lifetime of the product. Based on measurements to date, mobilization of mercury in CCRs in ash landfills, from leaching or gaseous release, appears to be low. However, the impact of advanced mercury emissions control technology (e.g., activated carbon injection) on beneficial use applications is uncertain. There is concern that the presence of increased concentrations of mercury or certain other metals, or high carbon content may reduce the suitability of CCRs for use in some applications (e.g., carbon content can limit use as replacement for Portland cement or as concrete admixture).

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Table 1. Mercury content of fuel fired in power plants in 1999. Source: Reference 2.

Fuel Type	Number of Samples	Hg content, µg/g dry basis	
		Mean	Range
Bituminous	27,793	0.11	0.0 – 1.3
Subbituminous	8,180	0.07	0.008 – 0.9
Lignite	1,047	0.11	0.02 – 0.75

Table 2. Distribution of mercury among scrubber outlet streams. Source: Reference 6.

Plant – Scrubber Type	FGD Byproduct[1]	Gypsum Fines[2]	Gypsum Fines Liquor[3]	Stack Gas
1 – Forced Oxidation	18.9%	7.8%	58.9%	14.4%
	7.3%	5.2%	65.6%	20.8%
2 – Forced Oxidation	48.1%	48.1%	0.0%	3.7%
3 – Inhibited Oxidation	65.7%			35.4%

[1]Calcium sulfate hemihydrate or gypsum produced by the FGD system
[2]Solid phase from hydroclone overflow stream sent to disposal
[3]Liquid phase from hydroclone overflow stream sent to disposal

Table 3. Results of leach testing analysis for coal fly ash from six facilities using ACI for enhanced Hg capture (Reference 8).

	Hg	As	Se
Total in CCR material (mg/kg)	0.1 -1	20 - 500	3 - 200
Leach results (µg/L)	Generally 0.1 or lower	<1 - 1000	5 – 10,000
MCL[1] (µg/L)	2	10	50
TC[2] (µg/L)	200	5,000	1,000
Variability relative to pH[3]	Low	Moderate to High	Moderate

[1]MCL is the maximum concentration limit for drinking water.
[2]TC is the toxicity characteristic and is a threshold for hazardous waste determinations.
[3] Variability defined as low is <1 order of magnitude difference; moderate is 1 to 2 orders of magnitude difference; and high is >2 orders of magnitude difference.

Table 4. Leach Data for Fly Ash (Reference 9).

	Hg	As	Se	Sb	Ba	B	Cd	Cr	Co	Pb	Mo	Tl
Total in Material (mg/kg)	0.04-0.6	70-90	2-30	3-15	600-1,500	NA	0.7-1.5	100-200	20-50	40-90	10-20	3-13
Leach results (µg/L)	<0.01-0.4	7-300	7-400	<0.3-200	90-4,000	200-300,000	<0.2-30	1-4,000	<0.3-200	<0.2-2	100-40,000	<0.3-300
MCL (µg/L)	2	10	50	6	2,000	7,000 DWEL	5	100	-	15	200 DWEL	2
TC (µg/L)	200	5,000	1,000	-	10^5	-	1,000	5,000	-	5,000	-	-
Variability relative to pH*	Low to High	Low to Med	Low to Med	Med to High	Low	Med to High	High	Low to Med	High	Med	Low to Med	Med

MCL - Maximum concentration limit for drinking water
TC - Toxicity Characteristic, threshold for hazardous waste determination
DWEL - Drinking water equivalent level

*Variability defined as
Low: <1 order of magnitude difference
Med: 1-2 orders of magnitude difference
High: >2 orders of magnitude difference

Note: Shaded areas indicated potential for exceeding thresholds for MCL and TC.

Table 5. Leach Data for FGD Gypsum (Reference 9) [Shaded areas indicated potential for exceeding thresholds for MCL and TC].

	Hg	As	Se	Sb	Ba	B	Cd	Cr	Co	Pb	Mo	Tl
Total in Material (mg/kg)	0.01-0.5	2-4	2-30	2-6	3-60	NA	0.3-0.5	6-20	1-4	1-12	2-12	0.6-2
Leach results (µg/L)	<0.01-0.6	0.5-10	4-3,000	<0.3-10	40-400	40-70,000	<0.2-50	<0.3-50	<0.2-10	<0.2-10	1-600	<0.3-20
MCL (µg/L)	2	10	50	6	2,000	7,000 DWEL	5	100	15	15	200 DWEL	2
TC (µg/L)	200	5,000	1,000	-	10^5	-	1,000	5,000	-	5,000	-	-
Variability relative to pH*	Low to Med	Low to Med	Low to Med	Low	Low	Low to Med	High	Med to High	Low	Low	Low	Low

MCL - Maximum concentration limit for drinking water
TC - Toxicity Characteristic, threshold for hazardous waste determination
DWEL - Drinking water equivalent level

*Variability defined as
Low: <1 order of magnitude difference
Med: 1-2 orders of magnitude difference
High: >2 orders of magnitude difference

Note: Shaded areas indicated potential for exceeding thresholds for MCL and TC.

FIGURE CAPTIONS

Figure 1. Distribution of mercury in FGD scrubber outflows at five bituminous coal-fired power plants with SCR and FGD. Source: Reference 3.

Figure 2. Distribution of CCR Applications by CCR Type Source: References 7 and 9.

Figure 3. Mercury concentration in fly ash and FGD gypsum samples. Source: References 8, 9, and 10.

Figure 4. Leach Data for Mercury as a Function of pH and Comparison to health-based levels for Fly Ash and Scrubber Sludge. Source: Reference 9.

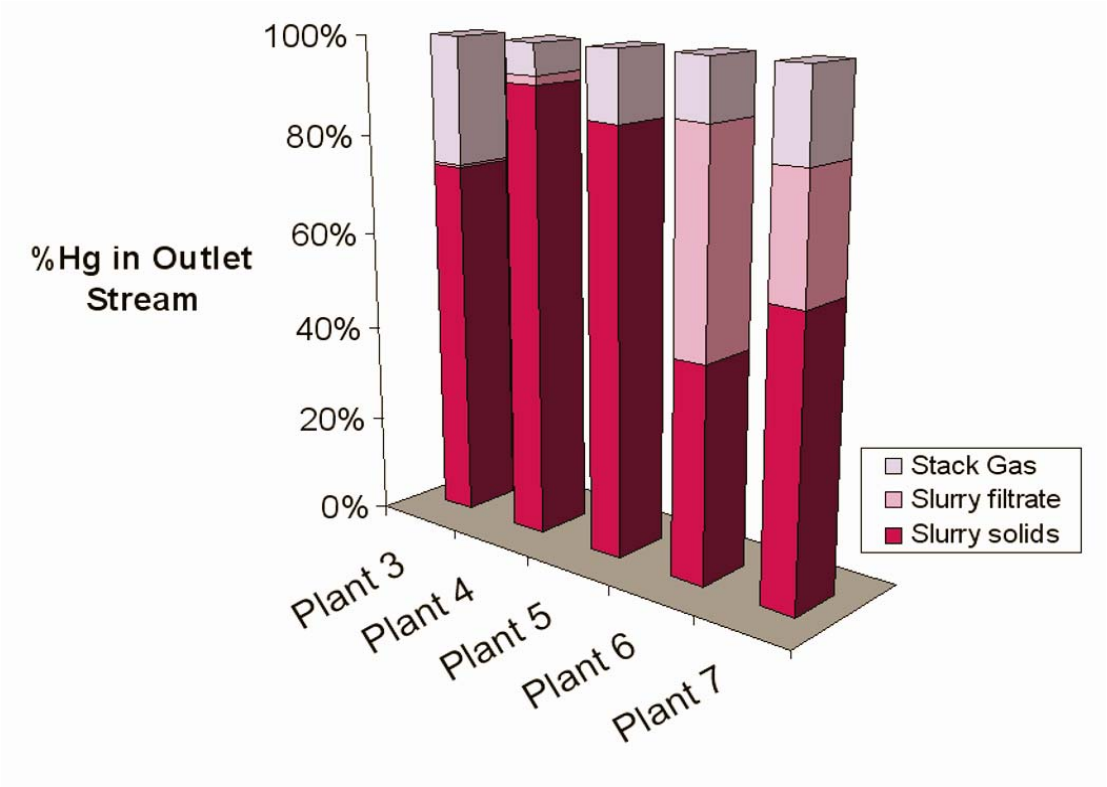
%Hg in Outlet Stream
100%
80%
60%
40%
20%
0%
Plant 3
Plant 4
Plant 5
Plant 6
Plant 7
Stack Gas
Slurry filtrate
Slurry solids

Fig. 1

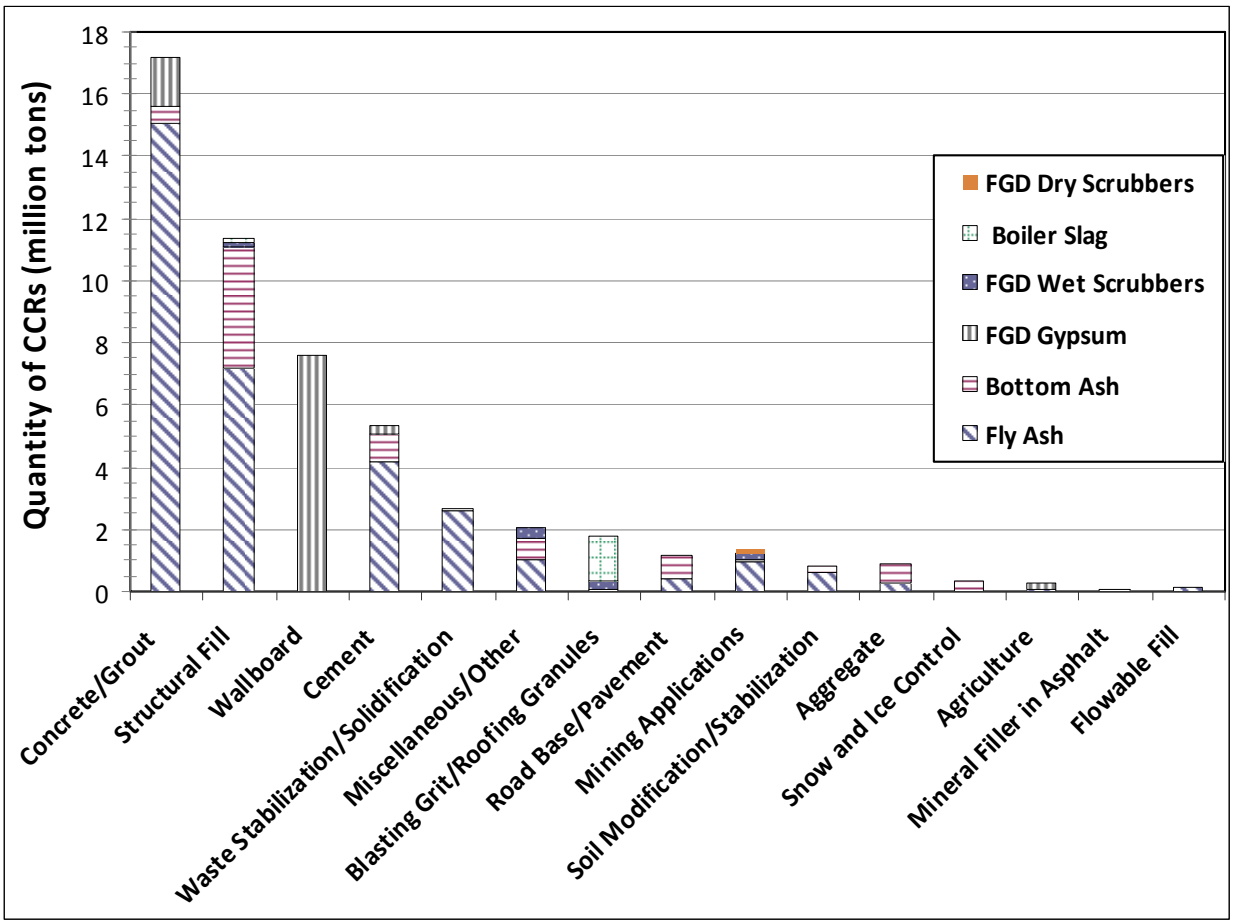
Quantity of CCRs (million tons)
18
16
14
12
10
8
6
4
2
0
FGD Dry Scrubbers
Boiler Slag
FGD Wet Scrubbers
FGD Gypsum
Bottom Ash
Fly Ash
Concrete/Grout
Structural Fill
Wallboard
Cement
Waste Stabilization/Solidification
Miscellaneous/Other
Blasting Grit/Roofing Granules
Road Base/Pavement
Mining Applications
Soil Modification/Stabilization
Aggregate
Snow and Ice Control
Agriculture
Mineral Filler in Asphalt
Flowable Fill

Fig. 2

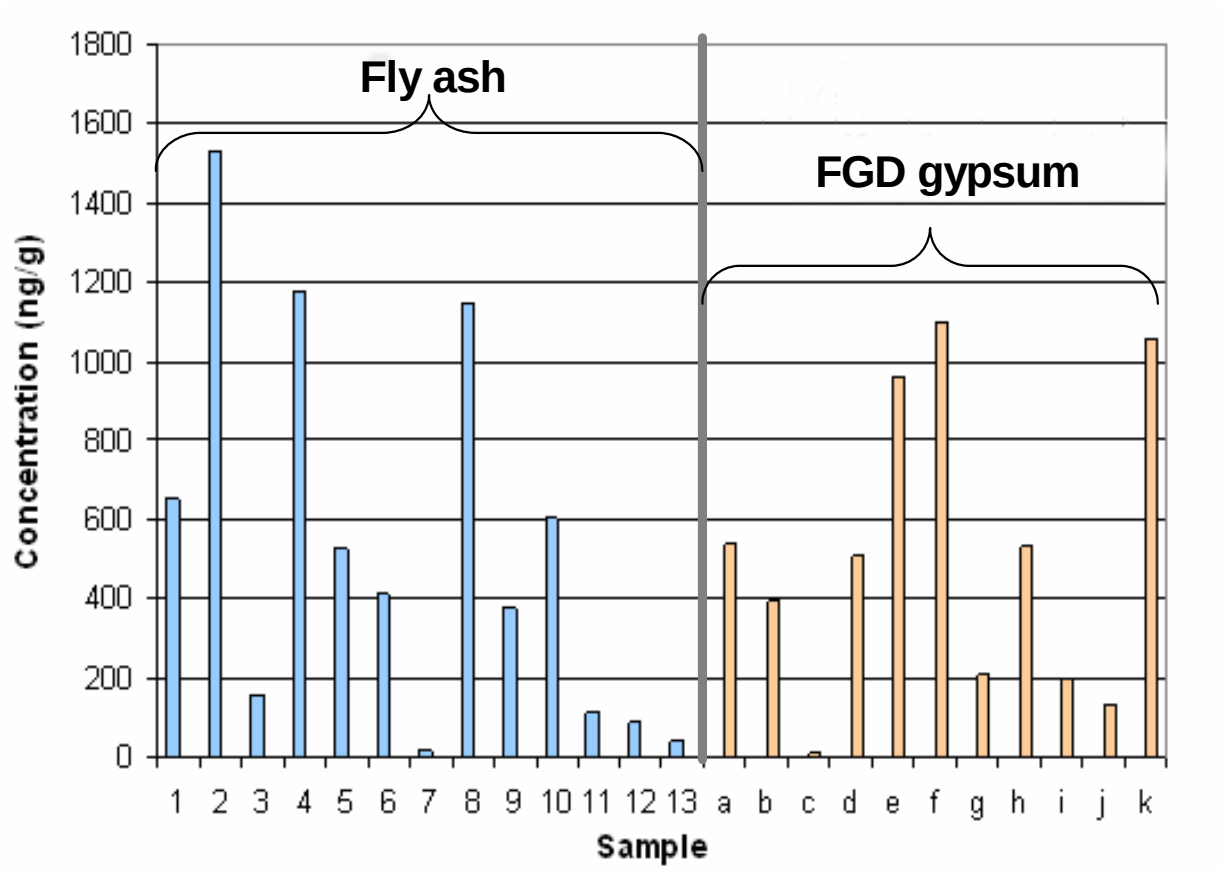
Fly ash
FGD gypsum
Concentration (ng/g)
1800
1600
1400
1200
1000
800
600
400
200
0
1 2 3 4 5 6 7 8 9 10 11 12 13 a b c d e f g h i j k
Sample

Fig. 3

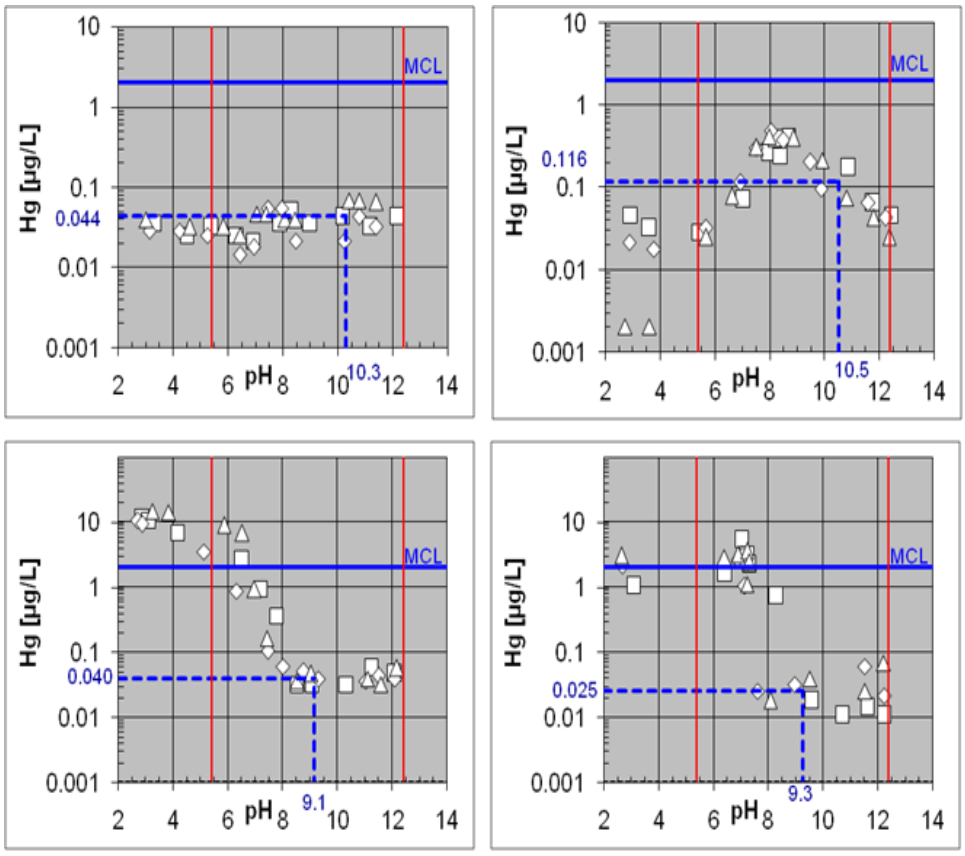
Hg [µg/L]
MCL
0.044
10.3
0.116
10.5
0.040
9.1
0.025
9.3
pH
Fly Ash
(Facility A, SNCR)
Scrubber Sludge
(Facility B, SCR)
No Post-Combustion NOx
Control in use
Post-Combustion NOx
Control in Use

Fig. 4.