



PDH-Pro.com

Mercury Contamination of Groundwater from Coal Ash

Course Number: CH-02-506

PDH: 1

Approved for: AK, AL, AR, FL, GA, IA, IL, IN, KS, KY, LA, MD, ME, MI, MN, MO, MS, MT, NC, ND, NE, NH, NJ, NM, NV, NY, OH, OK, OR, PA, SC, SD, TN, TX, UT, VA, VT, WI, WV, and WY

Author: Michael Kuznetz

New Jersey Professional Competency Approval #24GP00025600
North Carolina Approved Sponsor #S-0695
Maryland Approved Provider of Continuing Professional Competency
Indiana Continuing Education Provider #CE21800088
Florida Provider #0009553 License #868
NYSED Sponsor #274

This document is the course text. You may review this material at your leisure before or after you purchase the course. In order to obtain credit for this course, complete the following steps:

- 1) Log in to My Account and purchase the course. If you don't have an account, go to New User to create an account.
- 2) After the course has been purchased, review the technical material and then complete the quiz at your convenience.
- 3) A Certificate of Completion is available once you pass the exam (70% or greater). If a passing grade is not obtained, you may take the quiz as many times as necessary until a passing grade is obtained (up to one year from the purchase date).

If you have any questions or technical difficulties, please call (508) 298-4787 or email us at admin@PDH-Pro.com.





Mercury Contamination of Groundwater from Coal Ash

Abstract

Mercury is one of the trace metals found in coal combustion fly ash. Normally, it is not present in groundwater unless it leaches from coal fly ash storage lagoons, landfills and equipment containing mercury. Mercury speciation in coal changes to that in vapor, fly ash and later leachate that has a potential to leach into the aquifer vadose zone.

No significant research has been conducted to define leachate mercury boundary concentration as a function of coal combustion process variables for the purpose of groundwater plume delineation. This paper is the latest in a series of papers on mercury written by the author to assist the US EPA and US DOE in predicting mercury groundwater contamination extent. It presents a mathematical algorithm that defines initial mercury leachate concentration based on mercury mass law for inorganic aqueous species, flue gas sorbent injection rate and coal combustion process parameters. The reader is referred to the two preceding classes on mercury for additional details.

1. Introduction

Mercury is a hazardous air pollutant that circulates around the globe for a year before depositing back to the earth. Mercury emissions from electric power generation sources were estimated by the US Environmental Protection Agency (USEPA) to be 48 metric ton/yr in 1999, at the time constituting the largest anthropogenic source of mercury in the US. A new Maximum Achievable Control Technology standard for mercury under the Clean Air Mercury Rule was issued in 2005. Reduction in mercury emissions is directly associated with its transformation and accumulation onto a solid phase called Coal Combustion By-products (CCBs). CCBs containing fly ash are used in various products including Portland cement, concrete products, road bases, structural



Mercury Contamination of Groundwater from Coal Ash

fills, etc. A large amount of mercury-laden fly ash has been stored in various lagoons and landfills.

Albeit much research has been done on enhancing mercury removal from flue gas using sorbent injection technologies, no scientific research has focused on resulting groundwater mercury concentrations.

The most probable mode of mercury release from fly ash and transport to potable water supplies is aqueous transport via leachate and groundwater plume. Its initial leachate concentration is a function of coal ash mercury contents, activated carbon injection rate, combustion process temperature, air pollution control process configuration, fly ash pH, and leachate chloride and sulfate concentrations.

This paper describes an algorithm that can be used to determine the initial mercury leachate concentration from a coal combustion fly ash storage lagoon or landfill.

2. Derivation of Mercury Transformation Coefficient

In this paper, the Mercury Transformation Coefficient is the ratio of concentration of total mercury in fly ash produced by coal fired electric boiler utilities to that in the corresponding fly ash leachate. Mercury is present in coal in minute amounts. Very limited data exists on mercury extraction from coal combustion fly ash and resulting leachate concentration. The latter varies depending on the extraction procedure and fly ash pH. In the US, the most commonly used extraction procedures are TCLP (1) and SGLP (2) by the USEPA and USDOE, respectively. In these procedures, glacial acetic acid (weak acid) and distilled water, respectively, are used as extracts.



Mercury Contamination of Groundwater from Coal Ash

Unlike TCLP, SGLP results do not show correlation between heavy metal including mercury concentrations in fly ash and leachate. For this reason, TCLP results were used. Mercury extraction data for three fly ash matrixes from three different coals is discussed below.

2.1. Mercury Extraction Data Set A

Matrix 1 mercury leaching data is shown in Table 1.

Table 1. Set A

Sample No.	Activated Carbon Injection rate, lb/MMacf	Mercury concentration in fly ash, $\mu\text{g/g}$	Mercury leachate concentration, $\mu\text{g/L}$	
			TCLP	SGLP
1	1.5	10-50	0.01	BDL
2	1.5	10-50	N/A	BDL
3	1.5	10-50	BDL	BDL
4	10	0.5-5	BDL	BDL
5	10	0.5-5	BDL	BDL
6	10	0.5-5	BDL	N/A
7	0	0.2-0.53	BDL	0.01
8	0	0.2-0.32	0.02	0.05
9	10	0.4-1.4	0.07	0.03
10	10	N/A	0.03	0.01
11	20	0.4-1.4	BDL	0.01
12	20	N/A	0.02	0.02
13	0	0.1-0.7	0.034	BDL
14	10	0.1-0.7	BDL	BDL
15	10	0.1-0.7	BDL	BDL

BDL – below detection limit of 0.01 $\mu\text{g/L}$

N/A – not available

The available TCLP data in Table 1 is shown in Table 2 and Fig. 1. Table 3 shows the SGLP results.

Table 2. Mercury in fly ash vs. mercury in TCLP leachate for Set A.

Mercury in fly ash, $\mu\text{g/g}$		Mercury in TCLP
range	average	leachate, $\mu\text{g/L}$
0.2-0.32	0.26	0.02
0.4-1.4	0.9	0.07
0.1-0.7	0.4	0.034

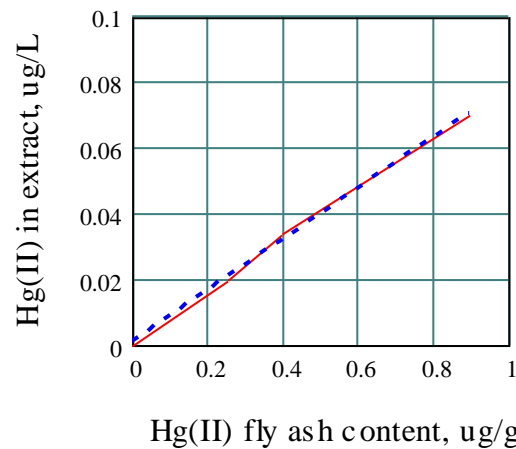


Figure 1. Plot of TCLP mercury extraction data for Set A.

The dashed line is a linear fit of the TCLP data in Table 2 which can be described as follows:

$$\text{Mercury extracted } (\mu\text{g/L}) = 0.078 \cdot (\text{ash mercury, } \mu\text{g/g}) + 0.0006142 \quad (1)$$

The correlation coefficient for the TCPL data in Table 2 is 0.999.

Table 3. Mercury in fly ash vs. mercury in SGLP leachate for Set A.

Mercury in fly ash, $\mu\text{g/g}$		Mercury in SGLP
range	average	leachate, $\mu\text{g/L}$
0.2-0.32	0.26	0.05
0.2-0.53	0.356	0.01
0.4-1.4	0.9	0.01
0.4-1.4	0.9	0.03

A plot of the average SGLP data in Table 3 is shown in Figure 2.

The dashed line is a linear fit of the SGLP data in Table 3 and described as follows:

$$\text{Mercury extracted } (\mu\text{g/L}) = 0.006437 \cdot (\text{ash mercury, } \mu\text{g/g}) + 0.017 \quad (2)$$

The correlation coefficient for the SGPL data in Table 3 is 0.129.

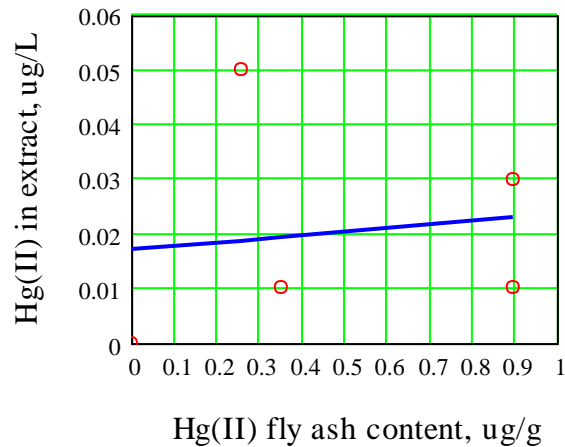


Figure 2. Plot of SGLP mercury extraction data for Set A.

2.2. Mercury Extraction Data Set B

Another research by the DOE/NETL on mercury in fly ash (7) that entailed column leaching studies on nine fly ash samples (3 from regular coal, 3 from pilot scale studies of activated carbon injection, and 3 from full scale activated carbon injection, ACI, tests) showed the following results.

Table 4. Set B.

Sample No.	Mercury in fly ash, mg/kg	Coal carbon, %	SGLP ng/L	TCLP ng/L	Sodium carbonate ng/L	Synthetic precipitate ng/L	Sulfuric acid ng/L	Control
FA50	1.096	1.31	22.80	48.00	56.80	21.20	22.60	ACI
FA53	1.04	2.45	4.60	20.10	6.50	17.50	15.70	ACI
FA56	1.07	1.89	13.70	22.10	27.10	4.40	8.70	ACI
FA52	92.07	28.66	4.40	116.00	37.80	6.60	7.80	ACI
FA55	1.38	16.08	222.00	36.70	1460.00	152.00	39.60	ACI
FA63	0.35	6.83	20.00	21.70	6.90	2.50	86.30	ACI
FA51	1.67	6.48	10.20	112.00	12.80	12.00	33.20	None
FA58	0.074	1.79	9.90	13.50	64.40	1.40	4.70	None
FA62	0.88	2.34	43.20	52.30	168.00	8.40	65.00	None

Table 5 shows correlation coefficients for fly ash mercury contents and the rest of the data in Table 4. Correlation between mercury concentration in fly ash and in TCLP leachate is 65.1 %. A linear fit of the TCLP data is shown in Figure 3. Correlation between mercury concentration in fly ash and in SGLP, sodium carbonate, synthetic precipitate, and sulfuric acid leachates is – 18.1, -12.7, -13.8, -30.7 percent, respectively. The pH values shown below the correlation coefficients indicate the hydrogen ion activities of the extracts.

Table 5. Correlation between mercury concentrations in fly ash and leachate.

Fly ash mercury mg/kg	Coal carbon contents	SGLP	TCLP	Sodium carbonate	Synthetic precipitate	Sulfuric acid
1.000	0.864	-0.181	0.651	-0.127	-0.138	-0.307
Extract pH		pH6.0	pH2.9	pH11.1	pH4.2	pH1.2

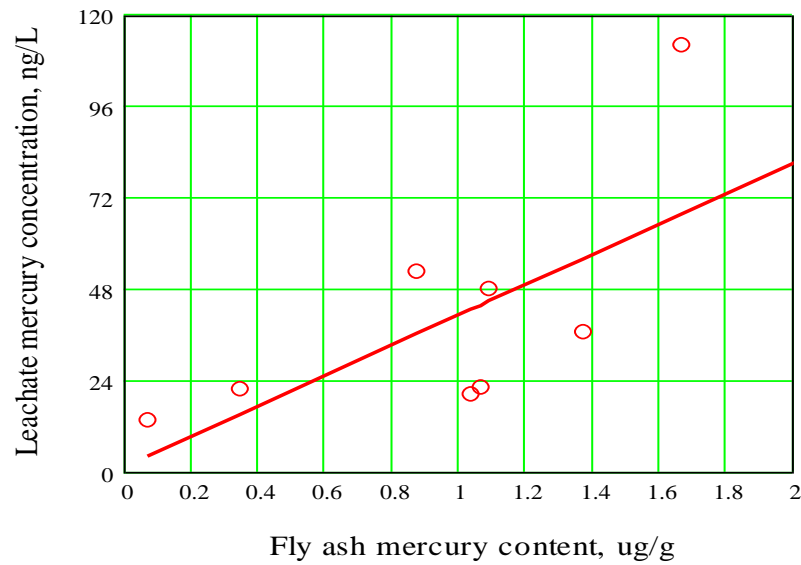


Figure 3. Plot of fly ash mercury content vs. TCLP leachate for Set B.

A linear fit in Figure 3 can be described by the following expression:

$$\text{Mercury extracted } (\mu\text{g/L}) = 0.04 \cdot (\text{ash mercury, } \mu\text{g/g}) + 0.00084 \quad (3)$$

2.3. Mercury Extraction Data Set C

Another study (8,9) on characterization and utilization of CCBs including coal combustion fly ash showed no visible correlation between the amounts of mercury in fly ash and leachate using both the TCLP and SGLP procedures. The extraction data is shown in Table 6. The data indicates no correlation between mercury concentrations in fly ash and SGLP extracts. Samples with the highest mercury concentrations in fly ash had the lowest concentrations in TCLP extracts. TCLP samples below mercury detection limit of $0.01 \mu\text{g/L}$ and those with the highest fly ash mercury contents were omitted from further analyses and the rest of the data was plotted in Figure 4.

Table 6. Set C.

Sample No.	Fly ash mercury μg/g	TCLP extract mercury, μg/L	SGLP extract mercury, μg/L
02-0.69	0.526	0.07	0.03
02-006	5.81	0.005	0.064
02-070	0.197	0.03	0.01
02-071	0.595	0.005	0.01
02-072	0.158	0.02	0.02
02-073	0.205	0.02	0.05
02-074	0.526	0.005	0.01
02-076	0.4	0.005	0.016
03-008	0.119	0.034	0.005
03-011	0.618	0.21	0.005
03-011	0.618	0.14	0.005
03-014	1.21	0.01	0.018

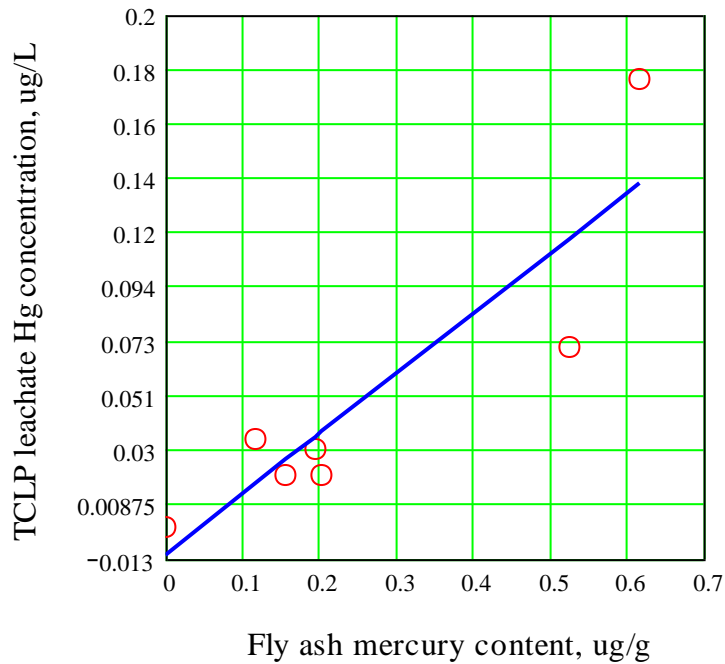


Figure 4. Plot of fly ash mercury content vs. TCLP mercury leachate content for Set C.

Correlation between the fly ash mercury content and the amount of mercury in leachate is 89.3%.

The linear fit of the TCLP data in Figure 4 is:

$$\text{Mercury extracted } (\mu\text{g/L}) = 0.235 \cdot (\text{ash mercury, } \mu\text{g/g}) - 0.011 \quad (4)$$

2.4. Average for Sets A, B, C

Table 7 shows the linear fit equations for the TCLP data sets A, B and C and the corresponding correlation coefficients. Equations 1, 3 and 4 show good positive correlation between mercury concentration in fly ash C_a ($\mu\text{g/g}$) and the corresponding TCLP leachate concentration C_s ($\mu\text{g/L}$).

Table 7. Average linear TCLP data fit and correlation.

Equation No.	Linear TCLP data fit	Correlation coefficient
(1)	$C_s = 0.078C_a + 0.0006142$	0.999
(3)	$C_s = 0.04C_a + 0.0008400$	0.651
(4)	$C_s = 0.235C_a - 0.0110000$	0.893

In Table 7, the series is represented by a limited number of fly ash sample sets with different pH, specific surface areas and different types of coals. Due to the lack of extraction data, the arithmetic average of the slopes and intercepts in Equations 1, 3 and 4 is the best approximation of the average linear fit for sets A, B and C:

$$\overline{C_s} = 0.1177C_a - 0.0095500 \tag{5}$$

The slope of this line defines the Mercury Transformation Coefficient as follows:

$$\text{Mercury in TCLP leachate } (\mu\text{g/L}) = 0.1177 \cdot (\text{fly ash mercury contents, } \mu\text{g/g}) \tag{6}$$

3. Mercury Phase Transformation Algorithm

The Mercury Phase Transformation Algorithm in this paper describes a relationship between mercury emission removal efficiency in electric utility boilers firing solid coal and the amount of mercury in fly ash leachate. Organically and inorganically (pyrite) bound mercury in coal is transformed into a gaseous phase during coal. The algorithm is applicable to all electric power

plants using activated carbon (AC) or other adsorbents for mercury emission control and can be adjusted to hazardous and medical waste incinerators using the procedure developed in the author's papers on mercury. Parts of the procedure can be used to develop similar algorithms for other metals such as cobalt, cadmium, barium, etc.

Besides AC, which is the most cost-effective sorbent for mercury control, fly ash-derived and silicate sorbents, chemically active silica and carbon aerogels (6) having a strong affinity for mercury have been used but to a much lesser extent than AC.

Mercury removal efficiency as a function of AC injection rate and process configuration, coal mercury and fly ash content and the Mercury Transformation Coefficient described by Eq. (6) are the parameters incorporated in the algorithm. The volume of bottom ash is negligible compared to the volume of fly ash. Mercury removal is defined by the Mercury Removal Efficiency Algorithm (Ref. 10):

$$RE = 100 \left(1 - e^{\frac{-H \cdot M}{G} \cdot \frac{398}{T^2 + 273} \cdot \frac{L^2 + A}{B}} \right) \quad (7)$$

where:

RE – total Hg removal efficiency, percent

H-activated carbon injection (ACI) rate, kg AC/Mm³ (standard dry air - flue gas)

M-total Hg adsorption capacity of activated carbon, g Hg_T/kg AC

G -concentration of total Hg in the flue gas, μg/m³ of standard dry air-flue gas

L - amount of unburned carbon in coal, percent wt.

T - temperature, °C

A - coefficient related to chlorine and sulfur coal contents, dimensionless

B - coefficient related to the APC process configuration, dimensionless.

Define Eq. (6) as follows:

$$1 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{L(\text{leachate})} = 0.1177 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{\text{g}(\text{fly ash})} = 0.1177 \cdot (\text{Hg}_T^{2+}, \text{ppm}) \quad (8)$$

Define a reciprocal of coal ash content and a removal efficiency, both in % as g(coal)/g(ash) and RE, respectively, and incorporate in Eq. (8) as follows:

$$1 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{L(\text{leachate})} = 0.1177 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{\text{g}(\text{fly ash})} \cdot \frac{\text{g}(\text{coal})}{\text{g}(\text{coal})} \quad (9)$$

Rearrange as follows:

$$1 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{L(\text{leachate})} = 0.1177 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{\text{g}(\text{coal})} \cdot \frac{\text{g}(\text{coal})}{\text{g}(\text{fly ash})} \quad (10)$$

Since $\frac{\text{g}(\text{fly ash})}{\text{g}(\text{coal})} = \frac{\text{coal ash content}(\%)}{100}$, (11)

Ratio transferred to fly ash = $\frac{\text{mercury removal efficiency}(\text{RE}, \%)}{100}$ and (12)

$$\frac{\mu\text{g}(\text{Hg}_T^{2+})}{\text{g}(\text{coal})} = \text{coal Hg}_T^{2+} \text{ content}(\text{ppm}) \quad (13)$$

Substitute Eq. (11, 12, 13) in Eq. (10):

$$1 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{L(\text{leachate})} = 0.1177 \cdot [\text{coal ash content}(\text{ppm})] \cdot \frac{100}{[\text{coal ash content}(\%)]} \cdot \frac{\text{RE}(\%)}{100} \quad (14)$$

Rearrange as follows:

$$1 \frac{\mu\text{g}(\text{Hg}_T^{2+})}{L(\text{leachate})} = 0.1177 \cdot \left(\frac{\text{RE}(\%)}{\text{coal ash content}(\%)} \right) \cdot [\text{coal Hg}_T^{2+} \text{ content}(\text{ppm})] \quad (15)$$

Simplify as follows:

$$C_0^{Hg} = 0.1177 \cdot \frac{RE}{C_{ash}} \cdot \{Hg_T^{2+}\} \quad (16)$$

Eq. (16) is the Mercury Phase Transformation Function in which the terms are specified in Eq. (15). The subscript “T” and superscript “2+” are total and divalent mercury, respectively. It can also be presented in the following form:

$$\text{air phase} \xrightarrow{\left(\frac{RE(\%)}{CAC(\%)}\right) \cdot \{Hg_{T.coal}^{2+}\}} \text{solid phase} \xrightarrow{0.1177 \left(\frac{g(ash)}{L(solution)}\right)} [Hg_T^{2+}]_{aqueous} \quad (17)$$

The Mercury Phase Transformation Algorithm, which specifies the initial leachate mercury concentration, is obtained by substituting Eq. (7) into Eq. (16) as follows:

$$C_0^{Hg} = 0.1177 \cdot \frac{100 \left(1 - e^{\frac{-H \cdot M}{G} \cdot \frac{398}{T^2 + 273} \cdot \frac{L^2 + A}{B}} \right)}{C_{ash}} \cdot \{Hg_{T.coal}^{2+}\} \quad (18)$$

A plot of Eq. (18) as a function of ACI rate is shown in Figure 5.

The plot entails the following conditions:

$G = 25 \mu\text{g}/\text{m}^3$ of standard dry air-flue gas
 $T = 50 \text{ }^\circ\text{C}$
 $M = 5 \text{ g Hg}_T/\text{kg AC}$
 $L = 5 \text{ percent}$
 $A = B = 100$
 $C_{ash} = 3\%$
 $\{Hg^{2+}\} = 2 \text{ ppm.}$

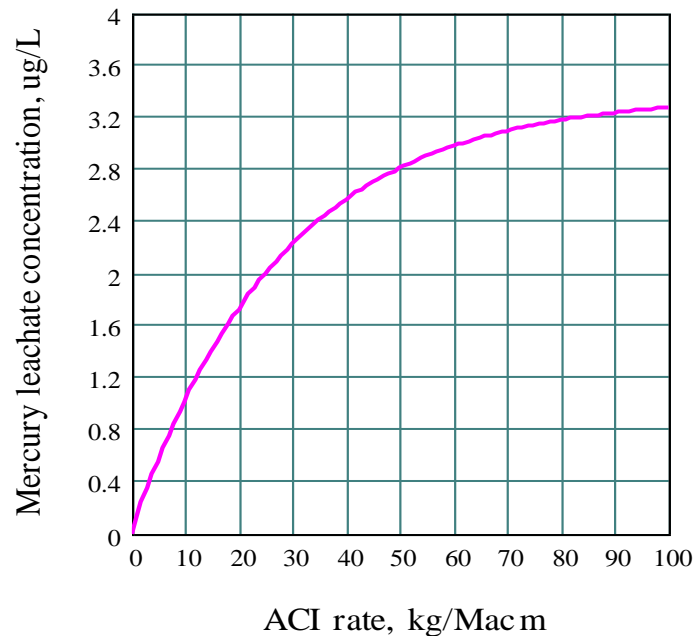


Figure 5. Plot of Mercury Phase Transformation Algorithm vs ACI rate.

4. Conclusion

Coal combustion fly ash, stored in various lagoons and landfills, contains large amounts of leachable mercury. It can travel via leachate to potable water supplies. The Mercury Phase Transformation Algorithm derived in this paper incorporates two mercury phase transformation algorithms, one from solid phase to air phase and the other from solid phase to liquid phase. A Monte Carlo simulation of Eq. (18) with a sample size of 5000, mercury coal content of 0.001 ppm-10 ppm (6,12,13), flue gas temperature from 170°F-300°F, coal fly ash content from 1% to 5%, mercury flue gas concentration from 1 to 100 $\mu\text{g}/\text{m}^3$ of standard dry air-flue gas and activated carbon injection rate from 1 to 100 kg/Macm showed a 70-percent probability that the initial mercury concentration in fly ash leachate exceeds 2 ppb (MCL). Whilst most of the potable water treatment technologies are capable of completely removing mercury during softening, flocculation, coagulation and filtering stages, there is a significant chance of aquatic habitats contamination.

References



Mercury Contamination of Groundwater from Coal Ash

- (1) U.S. Environmental Protection Agency. Toxicity Characteristic Leaching Procedure. *Federal Register*. 1990, 55(61), 11798-11877.
- (2) Hassett, D.J. *A generic test of leachability: The Synthetic Groundwater Leaching Method*. North Dakota Mining and Mineral Resources Institute, Grand Forks, ND, 1997.
- (3) Aljoe, W.W., Feeley III, T.J., Brickett, L.A., Scroeder, K. T., and Murphy, J. T. Environmental release of mercury from coal utilization by-products. *Ash*. 2005, 2-17.
- (4) Aljoe, W.W., Feeley III, T.J., Murphy, J.Y., Brickett, L. A. *The fate of mercury in coal utilization by-products*. DOE/NETL's Research Program, U.S. Department of Energy, National Energy Technology Laboratory: Washington, DC, 2003.
- (5) Butz, J., and Broderick, T. *Pilot testing of fly ash-derived sorbents for mercury control in coal-fired power plants*. ADA Environmental Solutions, LLC, Littleton, CO, 2001.
- (6) Keating, M.H., Maxwell, W.H., Driver, L., and Rodriguez, R. *Mercury Study Report to Congress*; EPA-452/R-97-010. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Washington, DC, 1997.
- (7) Kim, A. G., and Schroeder, K. *Factors controlling the solubility of mercury adsorbed on fly ash*. U.S. Department of Energy, National Energy Technology Laboratory: Pittsburgh, PA, 2005.
- (8) Pflughoeft-Hassett, D.F., Hassett, D.J., Heebink, L.V., and Buckley, T.D. *Mercury and air toxic element impacts of coal combustion by-product disposal and utilization*; Contract No. FY03-XLVIII-117; Energy & Environmental Research Center, University of North Dakota: Grand Forks, ND, 2001.
- (9) Pflughoeft-Hassett, D.F., Hassett, D.J., Laudal, D.L., and Pavlish, J.H. *Mercury release from coal combustion by-products to the environment*; 1999 International Ash Utilization Symposium; Energy & Environmental Research Center, University of North Dakota: Grand Forks, ND, 1999.
- (10) Kuznetz, M. *Universal Mercury Removal Efficiency Algorithm for coal-fired electric power plants*; PDH-PRO.com, 2019.
- (11) Morel, F.M.M., and Hering, J.G. *Principles and Applications of Aquatic Chemistry*; Wiley & Sons, Inc.: Hoboken, NY, 1993.
- (12) Shpirt, M.Ya. Transformation of mercury and its compounds upon coal processing. *Solid Fuel Chemistry*. 2002, 36(5), 58-68.
- (13) U.S. Environmental Protection Agency, Research and Development Office. *Control of mercury emissions from coal-fired electric utility boilers*; Interim report including ERRATA dated 3-21-02; EPA-600/R-01-109: Washington, DC, 2002.