The 2012 Atmospheric Mercury Monitoring Workshop & Regional Working Group Meeting on Environmental Information

Mercury Emission, Speciation and Distribution of Utility Boilers in Taiwan Burning Bituminous and Subbituminous Coal Blends

Hsing-Cheng Hsi[2*], Chien-Ping Chou[1,2], Chi-Ren Lan[3]

[1] Institute of Environmental Engineering and Management, National Taipei University of Technology, Taiwan

[2] Energy and Environmental Research Laboratories, Industrial Technology Research Institute (ITRI), Taiwan,

[3] Taiwan Power Research Institute, Taiwan Power Company, Taiwan

Introduction

Mercury: Why Is It of Interest?

- Unique physical and chemical properties
  - Hg^0: melting point = -39 °C, boiling = 357 °C, high saturation vapor pressure (0.246 Pa at 25 °C), easily vaporized at > 150 °C, low water solubility (6.0×10^{-5} g/L H_2O at 25 °C) 。
  - Existing in gaseous form in flue gases, difficult to be removed by conventional air pollution control devices.
- Highly toxic
  - Attack neuro-system
  - After absorption of mercury in the body, mercury circulates in the blood stream and accumulates in the spleen, liver, kidneys and bones.

Global Hg anthropogenic emissions

Table 3.7. Mercury by-product emissions from anthropogenic sources worldwide in 2005 (tonnes)(nb. values are rounded to 3 significant digits).

Region	Stationary combustion	Non-ferrous metals production	Pig iron and steel production	Cement production	Gold production	Mercury production (primary sources)	Waste incineration*	Caustic soda production	Other sources	Total
Africa	37.3	2.1	1.6	10.9	8.9	0.0	0.6	0.1	0.0	61.6
Asia (excluding Russia)	622	90.0	24.1	138	58.9	8.8	5.7	28.7	0.6	977
Europe (excluding Russia)	76.6	18.7		18.8	0.0	0.0	10.1	6.3	14.7	145
North America	71.2	5.7	14.4	10.9	12.9	0.0	15.1	6.5	7.2	144
Oceania	19.0	6.1	0.8	0.4	10.1	0.0	0.0	0.2	0.0	36.6
Russia	46.0	5.2	2.6	3.9	4.3	0.0	3.5	2.8	1.5	69.8
South America	8.0	13.6	1.8	6.4	16.2	0.0	0.0	2.2	1.5	49.6
World	880	141	45.4	189	111	8.8	35.0	46.8	25.5	1480

Source：http://www.chem.unep.ch/mercury/Atmospheric_Emissions/

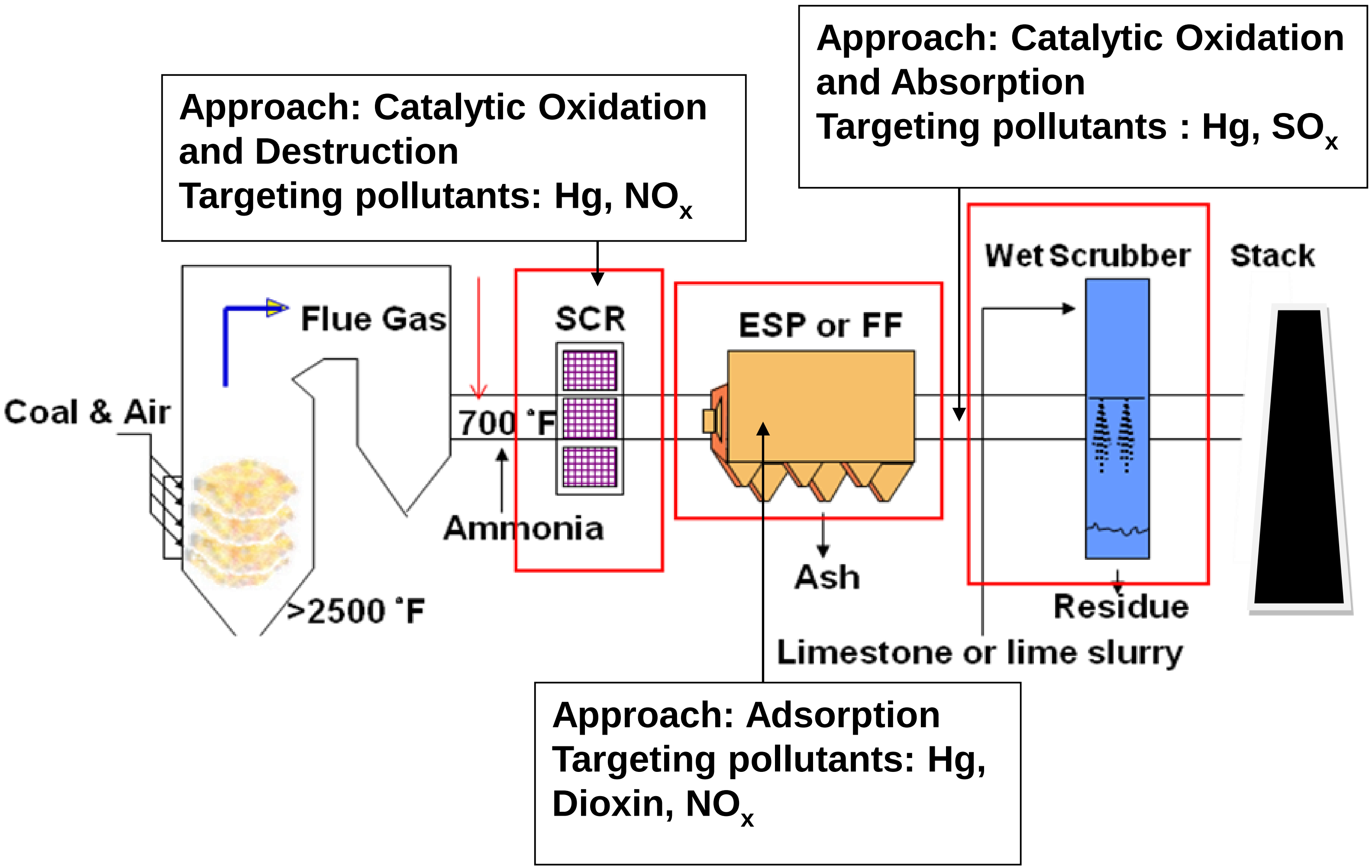
Hg emission of major stationary sources in Taiwan

Unit：metric ton/year

Source	2006	2007	2008	2009	2010
Municipal waste incinerator	0.233	0.244	0.250	0.260	0.168
Middle and small-size incinerator	0.009	0.010	0.011	0.011	0.028
Coal-fired power plant	**0.177**	**0.177**	**0.179**	**0.176**	**0.214**
Coal-fired steam-electric cogeneration plant	**0.140**	**0.143**	**0.222**	**0.170**	**0.248**
Cement kiln	0.269	0.242	0.196	0.182	0.171
Nonferrous smelter	0.029	0.031	0.030	0.028	0.028
Sinter plant	0.070	0.071	0.070	0.062	0.081
Electric arc furnace	0.190	0.218	0.215	0.169	0.175
Cyclone, bag house, precipitator ash	0.014	0.017	0.017	0.017	0.053
Other	0.176	0.187	0.192	0.198	0.199
Total	1.31	1.34	1.38	1.27	1.37

Control strategies

The success of Hg emission control using existing APCDs in CFPPs greatly relies on a thorough understanding of Hg speciation and distribution in the flue gases.



Objectives

- This study investigated the Hg speciation and distribution at a 300-MWh CFPP in Taiwan.
- The tested CFPP is equipped with low-NO_x burners for NO_x control, cold-side ESP for particulate capture, and wet FGD for SO_x removal.
- Samplings of all the relevant Hg inputs and outputs, including coal, lime, bottom ash/slag, fly ash, gypsum slurry and flue gases were performed. The Hg_p, Hg^0, Hg^{2+} concentrations/mass flow rates were measured and calculated. Mass balances for Hg throughout the entire power plant were subsequently obtained.

Significances

- These results provide a better understanding of the Hg emission, speciation and distribution across APCDs and can be further utilized to evaluate the environmental impacts of Hg emissions from CFPPs.
- These Data also help determining if a retrofit on existing APCDs or additional control strategies (e.g., adsorbent injection system) are needed for compliance of regulations, which may be implemented in the future.

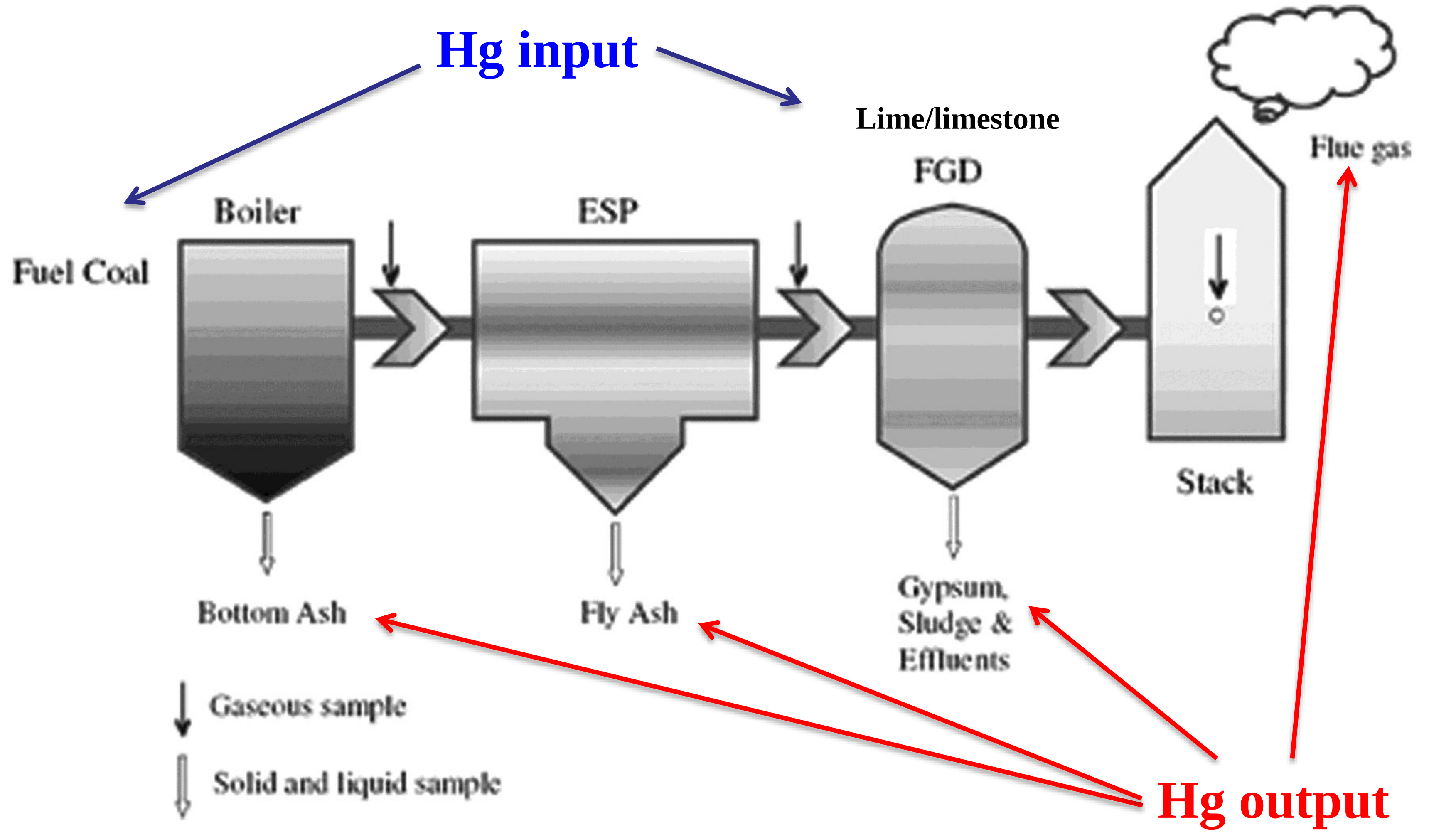
Methodology

1.Test Unit: a coal-fired utility boiler (#2) located in the Northern Taiwan

Load capacity	300 MW
Coal	Pulverized, blended Bituminous and Subbituminous coal
Particle control	Cold-side ESP
SO_2 control	FGD

Methodology

2.Sampling Locations：

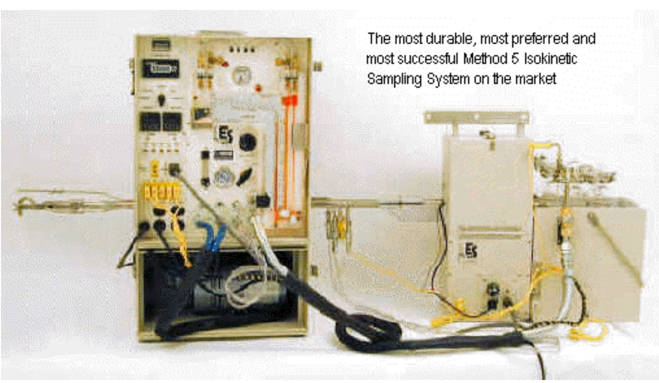


Two sampling campaigns were carried out in 2009 and 2010

Methodology

3. Sampling and Analysis Techniques：

- Ontario Hydro Method (OHM)
- U.S. EPA methods 7470A and 7471A (Liquid and Solid samples), CVAAS Hg analyzer



Methodology

4. Ontario Hydro Method (OHM)：

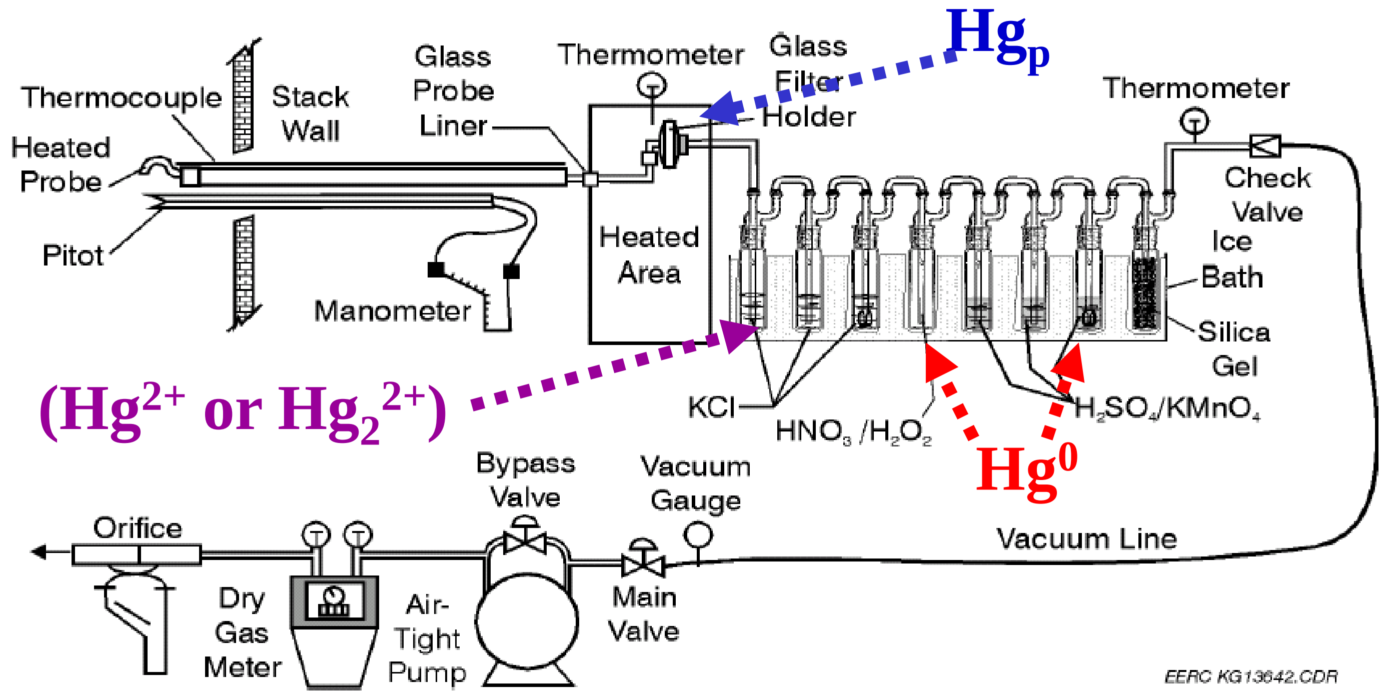


Figure 4-1. Diagram of sampling train for Ontario-Hydro Method (source: Reference 4).

Coal sample analytical results

- 2009: 20 coal samples, Indonesia (KPC) =15; Australia (Mac) =5.
  - Average Hg in Indonesia (KPC) = 0.037±0.005 mg/kg (0.025~0.044 mg/kg)
  - Average Hg in Australia (Mac) = 0.041±0.008 mg/kg (0.028~0.047 mg/kg)
  - Overall of the tested coal: **0.038±0.006 mg/kg** (0.025~0.047 mg/kg)
- 2010: 16 coal samples, Indonesia (KPC)=12; Australia (Mac)=4.
  - Average Hg in Indonesia (KPC) = 0.035±0.002 mg/kg (0.031~0.037 mg/kg)
  - Average Hg in Australia (Mac) = 0.025±0.007 mg/kg (0.020~0.035 mg/kg)
  - Overall of the tested coal: **0.033±0.006 mg/kg** (0.020~0.037 mg/kg)

Results indicate that the Hg content of coals used in the tested CFPP#2 boiler is similar and consistent.

Hg in inputs and outputs

- Hg is undetected in processing water (＜0.01 µg/L); FGD input water contained minor amount of Hg (20.6 µg/L), indicating that some of the Hg transported into recirculation water.
- Hg in lime was about 0.030 mg/kg and gypsum contained about 0.162 mg/kg of Hg, indicating that Hg accumulated in gypsum (2009 data). Hg in lime was about 0.036 mg/kg and gypsum contained about 0.111 mg/kg of Hg, again indicating that Hg accumulated in gypsum (2010 data).
- Bottom ash contained negligible amount of Hg(< 0.002mg/kg, 2009; 0.005 mg/kg, 2010). Fly ash contain significant amount of Hg (0.171 mg/kg, 2009; 0.175 mg/kg, 2010) .

CFPP#2 Hg distribution (2009)

Mercury Emission and Speciation Variation across APCDs[a]

Hg speciation	Inlet ESP		Inlet FGD		Stack	
	μg/Nm³	%	μg/Nm³	%	μg/Nm³	%
Hg_p	2.572	89.9	0.013	1.5	0.011	2.0
Hg^0	0.212	7.4	0.404	46.9	0.479	85.5
Hg^{2+}	0.077	2.7	0.446	51.7	0.070	12.5
Total Hg	2.861	100.0	0.862	100.0	0.560	100.0

[a] An average value of the five tests at the identical condition using the same mixed coal is presented.

CFPP#2 Hg distribution (2010)

Mercury Emission and Speciation Variation across APCDs[a]

Hg speciation	Inlet ESP		Inlet FGD		Stack	
	μg/Nm^3	%	μg/Nm^3	%	μg/Nm^3	%
Hg_p	1.935	69.3	0.007	0.4	0.004	0.6
Hg^0	0.853	30.5	0.731	48.9	0.623	97.0
Hg^{2+}	0.007	0.20	0.757	50.7	0.016	2.3
Total Hg	2.794	100.0	1.494	100.0	0.642	100.0

[a] An average value of the four tests at the identical condition using the same mixed coal is presented.

Control efficiency by APCDs

- The average total Hg removal was about 76% by existing APCDs, including (ESP and FGD). This result resembled the data reported by USEPA (between 29 and 74%).

Discussion on test results (based on 2010 data)

1. Hg Behavior in ESP and the Effect of Flue Gas Components

- In this study, high amount of Hg_p (69.3%) was measured, which may be due to the high unburned carbon in the fly ash that adsorbs the Hg.
- ESP removed 99.7% Hg_p; however, Hg^{2+} increased to 0.757 μg/Nm^3, indicating that catalytic oxidation of Hg^0 by flue gas component or fly ash occurred. This may be further enhanced by the environment of ESP (high-voltage discharge field).

Discussion on test results (based on 2010 data)

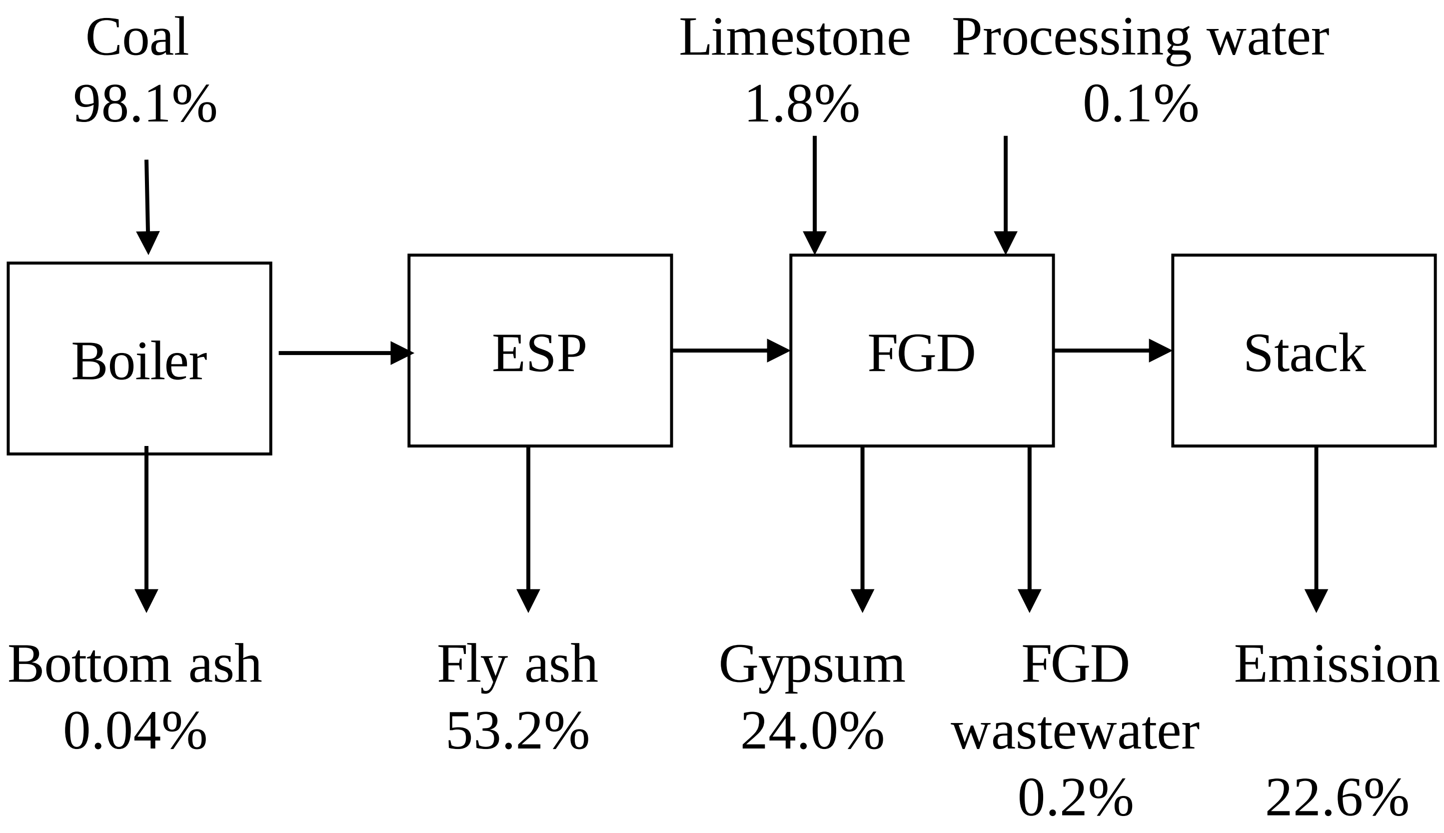
2. Hg Behavior in Wet FGD

- Wet FGD removed 98.0％ of dissolved Hg^{2+}; however, Hg^0 only decreased by 14.5% 。

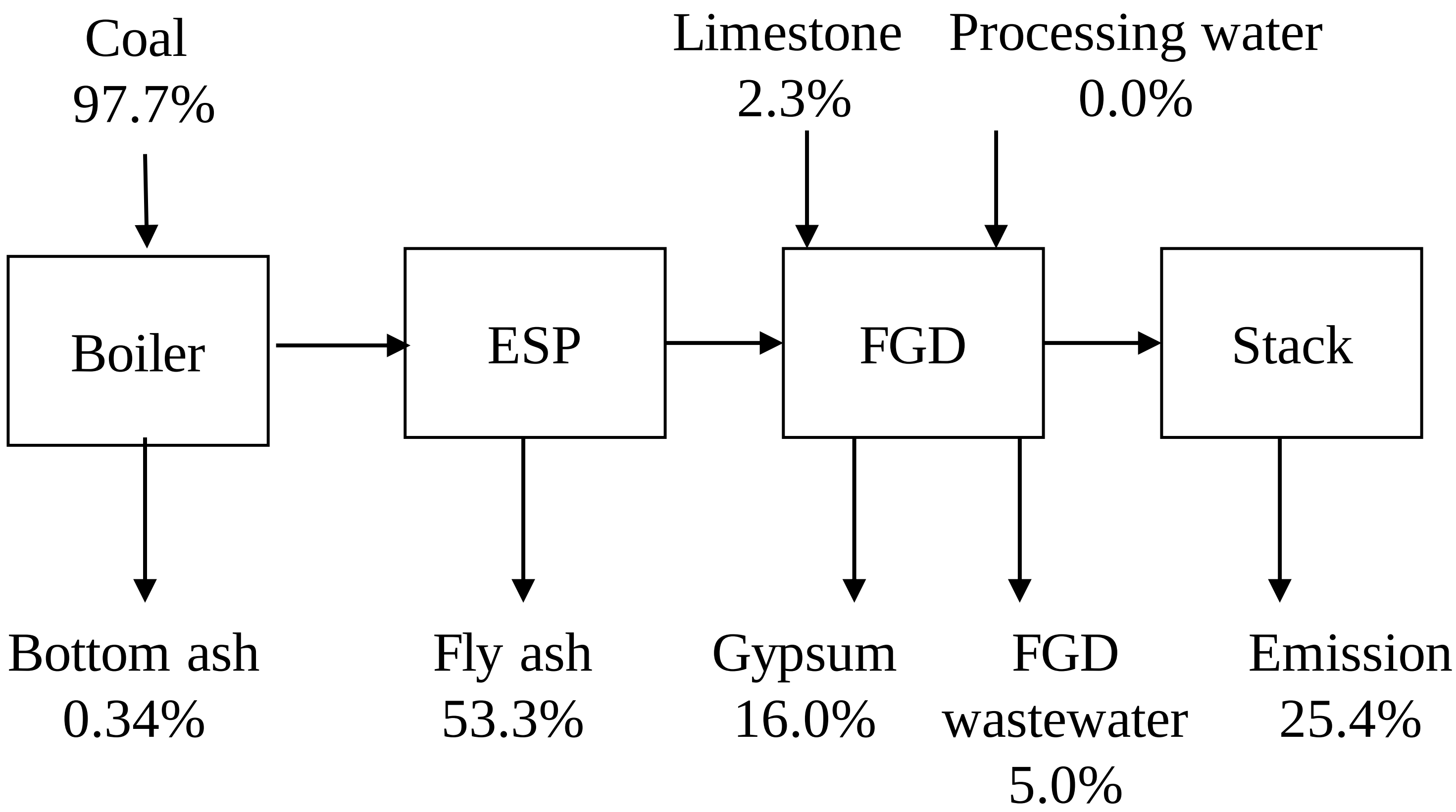
3 Mercury in Stack Emission

- Average Hg concentration in stack was 0.601 μg/Nm^3 (91.3%Hg^0，7.4％Hg^{2+} and 1.3％Hg_p), indicating that Hg^0 is the most difficult species to control.

CFPP#2 Hg distribution (2009)



CFPP#2 Hg distribution (2010)



Conclusion

- The Hg in coals for CFPP#2 boiler is similar.
- The major Hg source in the CFPP was **coal (97.8%),** with minor amount contributed from **lime (2.2%)**. **Fly ash is the largest Hg output (53.3%)**, followed by **stack emission (24.0%) and gypsum/FGD water(22.7%)** ，The overall mass balance disclosure was calculated to be approximately 85.4%.
- The Hg emissions from stack into the atmosphere was 0.601 μg/Nm^3 in average, Hg^0 , Hg^{2+}, and Hg_p occupied 91.3%, 7.4%, and 1.3%, respectively.

Acknowledgements

Financial support by the Taiwan Power Company is greatly appreciated.