Radisav, Vidic 5/20/25

WATER, AIR, & SOIL POLLUTION

an international journal
of environmental pollution

volume 56–1991

Kluwer Academic Publishers
Dordrecht / Boston / London

MERCURY
AS AN
ENVIRONMENTAL POLLUTANT

Refereed papers from the
International Conference held in
Gävle, Sweden, June 11–13, 1990

Guest editor

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THE FATE OF MERCURY IN COAL-FIRED POWER PLANTS AND THE INFLUENCE OF WET FLUE-GAS DESULPHURIZATION

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ABSTRACT. The Hg concentrations in coal as fired in power plants in the Netherlands are low, 0.2 $mg \bullet kg^{-1}$ on average. After combustion the Hg is released partly (between 1 and 98%, on average 42%) in a gaseous phase, which is finally emitted into the air. The other part of the Hg, which remains in the ash is separated from the flue gases by electrostatic precipitators. The variation of the vaporisation percentage of Hg is probably caused by the presence of two chemical forms: Hg^0 and $HgCl_2$. This may be concluded from the observation that relatively high concentrations of HCl in the flue gases ($\approx$150 $mg \bullet m^{-3}$) give rise to low Hg concentration in the vapor phase. In cases when the concentrations of HCl are relatively low ($\approx$25 $mg \bullet m^{-3}$) the amount of Hg in the vapor phase is high. The average gas phase concentrations of Hg in the flue gases, based on 33 measurements with no FGD, is 4.1 $\mu g \bullet m_o^{-3}$. In a wet FGD based on the lime/limestone-gypsum process 50 to 70% of the Hg in the flue gases is removed, leaving a residual concentration of 1-2 $\mu g \bullet m_o^{-3}$. The emission factor is then about 0.5 $mg \bullet GJ^{-1}$ or 5 $\mu g \bullet kWhr^{-1}$. In one particular measuring serie the fate of Hg was studied in a FGD-installation with a prescrubber.

1. Introduction

About 40% of the electricity in The Netherlands is generated by coal. Only imported bituminous coal is fired in pulverized dry-bottom boilers equipped with high efficiency electrostatic precipitators (ESP). Today all large boilers are also equipped with wet flue-gas desulphurization (FGD). Trace elements are an important environmental aspect. Extensive measurements were performed in the past decade at Dutch coal-fired power plants in order to establish the fate of the trace elements. These measurements were carried out by KEMA (Joint Laboratories and Other Services of The Dutch Electricity Supply companies), in cooperation with ECN (The Netherlands Energy Research Foundation). This paper will focus on the results concerning Hg.

Most trace elements end up in the ash, about 99.9% of which is collected as bottom ash

Water, Air, and Soil Pollution **56**: 21–33, 1991.

(12%) and as pulverized fuel-ash (PFA) (88%). Accordingly the emissions into the air are very low (Meij *et al.*, 1985; Meij *et al.*, 1989). For Hg however the situation is different. During combustion, Hg in the coal is released partly as a gas. The adverse effect is that a considerable proportion of the Hg stays in the vapor phase in the flue gases and is released into the air. The introduction of wet FGD reduces these Hg emissions.

In this paper the amount of Hg introduced by coal and the fate of the Hg in the power plant, including the removal in the FGD, is quantified.

2. Material and Methods

Flue gases were sampled at a flow of 1 L•min^{-1}; on activated carbon in a cartridge with two compartments, each with a diameter of 10 mm and a length of 50 mm, at a temperature of about 60°C. Aerosols were separated by a plane teflon filter. Spherical activated carbon of KUREHA was used (grade: BAC MP, diameter 0.1 to 1 mm)(Meij *et al.*, 1989; Meij, 1991). These measurements are indicated in Table II as C_2. In the years 1981 and 1982 a preliminary design of the cartridge was used (in the stack with a cellulose acetate filter), indicated in Table II as C_1. In some cases flue gases were sampled in three successive Greenburg-Smith impingers, at a flow of 13 L•min^{-1} containing 50 mg•l^{-1} $KMnO_4$ in 10% H_2SO_4 or 4% $K_2Cr_2O_7$ in 4 M HNO_3 (indicated in Table II by I) or by three De Graaff wash-bottles at a flow of 1-2 L•min^{-1} containing 4% $K_2Cr_2O_7$ in 4 M HNO_3 (indicated in Table II by W). Each system was preceded by an impinger or wash-bottle containing 2% H_2O_2 in order to remove SO_2. The impinger method was used as prescribed by EPA (Shendikar *et al.*, 1984). The wash bottle method was used as described by Dumarey *et al.*, 1981.

The solid samples were digested using HNO_3-HF at 180°C in a pressurised teflon-lined decomposition vessel according to NVN 2507. Hydrid Generation Atomic-Absorption Spectroscopy was used for chemical analysis. The activated carbon was analyzed by Instrumental Neutron-Activation Analyses (INAA). In some coal and ash samples with very low Hg concentrations the following procedure was applied in order to obtain results with an accuracy of ± 1 µg•kg^{-1} (series I, II, IV, IXd-IXi): after irradiation with neutrons a preconcentration was performed whereby the samples were heated in a quartz tube in a nitrogen atmosphere (<950°C) and the Hg vapor, collected on activated carbon, was measured with gamma spectrometry (Sloot and Zonderhuis, 1979; Sloot and Das, 1974).

3. Results and discussion

3.1 COAL

The results for 37 coal samples, which were analyzed for Hg, are presented in Table I. Mostly samples were taken during measuring series, the results of which are also given in Table II. Sampling took place after milling, so that homogeneous samples were

Table I. Hg in coal as imported in the Netherlands (one value per lot)

origin	concentrations in mg•kg^{-1}	n	x	s	v(%)
Australia	0.033, 0.03, 0.04, 0.047, 0.068, 0.095, 0.1, 0.12, 0.25	9	0.087	0.069	79
USA(east)	<0.5, <0.2, 0.09, 0.1, 0.15, 0.22, 0.25, 0.51	6	0.22	0.16	71
Columbia	0.04, 0.04	2	0.04		
Poland	0.14, 0.16, 0.80, 1.78	4	0.72	0.77	107
Ruhr Area	0.16	1	0.16		
blend	<0.08, <0.2, 0.036, 0.043, 0.062, 0.093, 0.1, 0,1, 0.1, 0.12, 0.19, 0.21, 0.29	11	0.12	0.08	64
total		33	0.20	0.32	162
weighted average for 1981/1982[1]			0.24		
weighted average for 1988[2]			0.16		
weighted average for 1989[3]			0.17		

n: number, x: average value, s: standard deviation, v: coefficient of variation

[1] Australia: 30%, USA: 50%, Poland: 13%, W.Germany 7%

[2] Australia: 42%, USA: 22%, Colombia: 19% and Poland: 8%

[3] Australia: 34%, USA: 31%, Colombia: 22% and Poland: 8%

obtained. Homogeneity was achieved by:

- the smaller particle size (<100 µm),
- the removal of large fragments consisting of pyrite from the raw coal in the mills,
- the grinding process.

Also, more homogeneous samples were obtained at the power plant as compared with mine samples as a result of the various handling processes during transportation from the mine by train, sea-vessel and river-vessel to the power plant, the stacking processes, and finally the reclaiming processes in the trench bunker of the power plant.

In series VI nine samples from one lot were taken during the week. The results are presented in Fig. 1. By taking the concentration level into consideration, the coefficient of variation of Hg in one lot is low, (v=40%).

The average concentrations of coal imported from the same countries were calculated and are listed in Table I. The lowest concentrations were found in coal from Australia and Colombia. Higher concentrations were found in coal imported from the eastern part of the USA. The highest concentrations were found in coal imported from Poland.

In general the concentrations are low (< 0,1 mg•kg^{-1}) and the range is narrow (0,03 to 0,3 mg•kg^{-1}). The average value is 0.20 mg•kg^{-1}. Chemical laboratories were often contaminated with Hg and therefore the values as reported in literature from the past are probably too high. For 1981/82 a weighted average for the coal fired in the Netherlands on the basis of the origin of the coal is 0.24 mg•kg^{-1}, for 1988 it is 0.16 mg•kg^{-1} and for 1989 0.17 mg•kg^{-1}.

The highest values of >0.1 mg•kg^{-1} were essentially found in samples from 1982 and

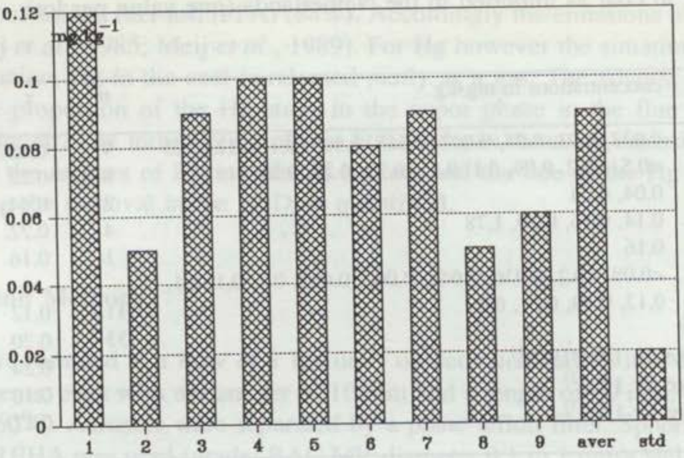

Fig. 1. The variation of Hg in coal within one lot (eastern USA).

1983, which were mostly raw coal samples. The concentrations in samples after 1983 are nearly all below 0.1 $\text{mg}\bullet\text{kg}^{-1}$. It is not clear whether this is caused by improved analytical procedures, by differences between raw and pulverized coal or by a real decrease in concentrations. Such a decrease might be accomplished by better cleaning processes at the mines. If the 1982 values are not included, the average values would be lower.

The results presented are in agreement with work done in Sweden on coal from the same origin. This other study was carried out in the framework of the Coal-Health-Environmental Project (average 0.1 $\text{mg}\bullet\text{kg}^{-1}$) (KHM, 1983). The figures for US coal are in agreement with the median value for eastern US coal as given by the Illinois State Geological Survey (0.17 $\text{mg}\bullet\text{kg}^{-1}$) (Gloskuter *et al.*, 1977).

3.2 MASS BALANCES IN POWER PLANTS

3.2.1 *Introduction.* Thirty six measurements were performed at 11 different boilers, firing coal from Australia, USA, Poland, Colombia and blends. The results are presented in Table II. Some larger scale tests lasted several days and included measurements of all streams. In those cases a complete mass balance could be established (see Table III). Most measurements included only the coal and the Hg vapor in the flue gases after the electrostatic precipitator (ESP).

To describe the enrichment of Hg in the ash with respect to the coal, the term relative enrichment (RE) is used:

$$\text{RE} = \frac{[\text{conc. Hg in ash}]}{[\text{conc. Hg in coal}]} \bullet \frac{[\text{ash content coal in \%}]}{100} .$$

This means that if the RE factor is equal to one, all the Hg originally present in the coal is concentrated in the ash that remains after combustion.

3.2.2. *Bottom Ash.* It appears that Hg evaporates during the combustion process and is carried along with the flue gases. It is believed that Hg is most probably present in elemental state (Klein *et al.*, 1975; Kaakinen *et al.*, 1975). The coarse ash particles (> 100 µm) immediately fall to the bottom of the boiler and are called bottom ash or slag. Since contact with the flue gases is limited, the concentration of Hg in the bottom ash is very low and mostly below the limit of detection. In two series the exact concentration could be established (RE=0.1) and about 2% of the Hg originally present in the coal is found in the bottom ash.

3.2.3. *Pulverized-Fuel Ash.* The remaining fly-ash particles and the Hg vapor follow the route of the flue gases via the air preheater, ESP and, if no flue-gas desulphurization is present, are released into the air via the stack. The temperature of the flue gases decreases to about 350°C upstream the air preheater and to about 125°C in the ESP. Somewhere on this route Hg vapor might condense on the fly-ash particles or adsorption might occur. If such is the case, the concentrations of Hg will increase in the smaller particles. For this reason the concentration of Hg in the pulverized-fuel ash (PFA or collected ash in the ESP) as collected in the four successive hoppers of the ESP, was studied. Going from hoppers 1 to 4, the particle size decreases. For instance, test series IV the mass median diameter (MMD) decreases from 22 via 13 via 7 to 7 µm (Meij *et al.*, 1990). However, from Table II it can be deduced that such an increase in concentration is found to be very slight. The values vary more or less at random. The results of series IV and XIV are presented in Fig. 2. Probably at that temperature (120 to 140°C) the Hg has a high volatility and after adsorption it will be readily vaporized again. For mass balance studies only the PFA from the collection tank is important. If such a figure is absent, the mean value of PFA-1 and PFA-2 have to be taken into consideration, because they constitute about 90% of the collection tank. The RE-factor of the PFA varies between 0.1 and 0.4. As a part of the mass balance the contribution of the PFA varies between 7 and 43%.

A contribution of about 10% is expected by taking into consideration the high volatility of Hg, as is found in series IV and XII. This anomaly will be further discussed in the next section.

3.2.3. *Flue Gases After ESP.* The Hg present in the aerosol is negligible (concentrations <1 $mg \bullet kg^{-1}$) and the particulate loadings after ESP for the Netherlands are 20 $mg \bullet m_0^{-3}$ on average (Meij *et al.*, 1985). This means that the contribution of Hg in the flue gases is dominated by the Hg vapor, which will exclusively be taken into consideration. In 33 measurements, the gaseous Hg concentrations in the flue gases were found to be between 0.3 and 35 $\mu g \bullet m_0^{3}$, with a mean value of 4.1±5.8 $\mu g \bullet m_0^{3.}$ This means an annual emission of 50 kg Hg at a 600 MW(e) coal-fired power plant without a FGD unit and at 5700 hrs a year at full load.

Table II. Survey of Hg measurements performed at power plants in the Netherlands (in coal, bottom ash, pulverized-fuel ash (PFA) and flue gases after ESP)[1]

	date	origin coal[2]	power plant	ash cont. %	Hg content in mg•kg^{-1}								vapor phase[4]		
					coal	bottom ash	PFA-C	PFA-1	PFA-2	PFA-3	PFA-4	fly-ash	conc. µg•m$_o^{-3}$		%
I	80-02	AUS/RU	CG-11	13.8	0.062	-	0.2 (0.4)	-	-	-	-	0.5 (1.1)	-	-	
II	80-06	PO	AC-8	15.1	0.14	0.1 (0.1)	0.35[3] (0.4)	0.25 (0.3)	0.56 (0.6)	-	-	1 (1.1)	-		-
III	81-10	USA	CG-12	11.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		35	C_1	>67
IV	81-02	AUS	AC-8	12.9	0.030	0.021 (0.08)	0.018 (0.1)	0.052 (0.2)	0.014 (0.1)	0.016 (0.1)	0.061 (0.2)	<1 (<3.7)	2.5	C_1/I	67
V	82-10	USA/PO	AC-8	13.2	<0.08	-	-	-	-	-	-	-	2.7	C_1/W	>34
VI	83-03	USA	AC-5,8	13.9	0.09	-	-	-	-	-	-	-	-		-
VIIa	84-09	USA	AC-4	8.3	<0.2	-	-	-	-	-	-	-	1-3	C_2/W	-
VIIb	84-09	USA	AC-8	8.3	<0.2	-	-	-	-	-	-	-	1-4	C_2/W	-
VIII	84-10	CAN/PO	AC-8	11.5	<0.2	-	-	-	-	-	-	-	1-2	C_2/W	-
IXa	82-01	AUS	CG-11	-	0.1	-	-	-	-	-	-	-	2.7	I	27
IXb	82-01	BLE	CG-11	-	0.1	-	-	-	-	-	-	-	2.5	I	25
IXc	82-01	USA/RU	CG-11	-	0.1	-	-	-	-	-	-	-	0.5	I	5
IXd	82-01	PO	CG-11	-	0.16	-	-	-	-	-	-	-	8.5	I	53
IXe	82-02	BLE	CG-11	-	0.29	-	-	-	-	-	-	-	3.2	W	11
IXf	82-02	BLE	CG-11	-	0.21	-	-	-	-	-	-	-	4.6	W	22
IXg	82-03	PO	CG-11	-	1.78	-	-	-	-	-	-	-	1.6	W	1
IXh	82-03	PO/RU	CG-11	-	0.19	-	-	-	-	-	-	-	1.7	W	9
IXi	82-05	BLE	CG-11	-	0.12	-	-	-	-	-	-	-	0.3	W	3
IXj	82-10	PO	CG-13	12.5	-	-	-	-	-	-	-	-	2-9	C_1/W	-
X	85-12	AUS	AC-8	9.6	0.02	<0.25	<0.25	<0.25	<0.25	<0.25	-	-	1-2	C_2	75
XI	86-05	USA	AC-8	13.0	0.17	-	-	0.4 (0.3)	-	-	0.7 (0.5)	-	6.3	C_2	39
XII	86-06	USA	CG-13	11.8	0.08	-	-	0.07 (0.1)	-	-	-	-	3.4	C_2	87
XIIIa	87-09	AUS	AC-8	12.5	<0.2	-	-	-	-	-	-	-	4	C_2	
XIIIb	87-09	AUS	AC-8	10.2	0.03	<0.1	-	0.06 (0.2)	0.28 (0.7)	0.11 (0.4)	0.1 (0.3)	-	2	C_2	67
XIV	87-10	CO	AC-8	12.7	0.04	<0.1	-	0.07 (0.2)	0.13 (0.3)	0.36 (1.1)	0.13 (0.4)	-	2.2	C_2	55
XVa	88-04	AUS/CO	AC-4	10.5	0.036	-	-	-	-	-	-	-	1.7	C_2	44
XVb	88-04	AUS/CO	AC-5	9.9	0.037	-	-	-	-	-	-	-	2.4	C_2	61
XVc	88-04	AUS	AC-8	15.5	0.068	-	-	-	-	-	-	-	6.2	C_2	84
XVd	88-03	AUS	BS-12	9.9	0.047	-	-	-	-	-	-	-	5.5	C_2	98
XVe	88-06	AUS/CO	MV-2	11.5	0.043	-	-	-	-	-	-	-	2.2	C_2	48
XVf	88-03	BLE	CG-11	8.6	0.103	-	-	-	-	-	-	-	2.9	C_2	27
XVg	88-03	BLE	CG-12	8.9	0.1	-	-	-	-	-	-	-	2.9	C_2	29
XVh	88-03	BLE	CG-13	9.9	0.093	-	-	-	-	-	-	-	2.6	C_2	26
XVi	88-04	AUS	MC-4	14.0	0.097	-	-	-	-	-	-	-	5.3	C_2	49
XVj	88-04	AUS	MC-5	13.1	0.089	-	-	-	-	-	-	-	6.3	C_2	62
XVk	88-04	AUS	MC-6	8.2	0.1	-	-	-	-	-	-	-	1.8	C_2	18
number				27	30	5	7	6	4	3	4		33		26
average				11.5	0.15	<0.1	0.21	0.15	0.25	0.16	0.25	<1	4.1		42
standard deviation				2.1	0.31		0.12	0.14	0.24	0.18	0.30		5.8		28
coefficient of variation			(%)	19	207		58	96	96	110	122		141		66

[1] In brackets the relative enrichment (RE) factor, PFA is pulverized-fuel ash as collected in the ESP, the numbers 1 to 4 indicate the successive hoppers 1 to 4 of the ESP, C indicates the total collection tank of the ESP, which contains the ash from hoppers 1 to 4

[2] AUS: Australia, RU: Ruhr area in West Germany, PO: Poland, USA: United States of America (eastern part), CAN: Canada, CO: Colombia, BLE: blend of more than two lots

[3] results derived from fly ash sampled in the flue gases before ESP

[4] sampling method of gaseous Hg: I: impinger, W: wash bottles, C_1: activated carbon cartridges in stack (≈130°C), C_2: activated carbon cartridges out of stack (≈60°C); % is related to the amount of gaseous Hg relative to the Hg original present in the coal.

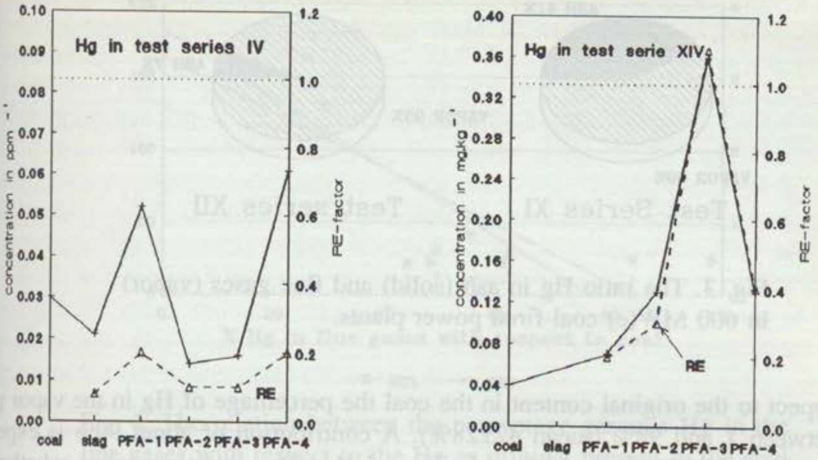

Fig. 2. The Hg concentrations in coal and the corresponding ash: slag and PFA as collected in the four successive hoppers of the ESP, together with their relative enrichment factor. The particle size of the PFA decreases going from hopper 1 to 4.

Table III. Mass balances of Hg in 600 MW(e) coal-fired power plants[1)]

test serie	in coal	out bottom ash	PFA	gaseous	mass balance out/in
in $g.h^{-1}$, in brackets in % (in which the measured output is assumed to be 100%):					
IV	AUS 6	0.1 (2)	0.4 (7)	5 (91)	0.8
X	AUS 3.7	2)	<3.9	2.8	<1.8
XI	USA 31.6	2)	8.5 (41)	12.1 (59)	0.7
XII	USA 15	2)	1 (10)	13 (90)	0.9
XIIIb	AUS 5.6	2)	2.8 (43)	3.7 (57)	1.2
XIV	CO 7.4	2)	1.5 (27)	4.1 (73)	0.8

[1)] the contribution of the aerosol-bound Hg (the fly ash) as present in the flue gases after ESP is negligible

[2)] the concentrations are below the detection limit and hence their contribution is ignored.

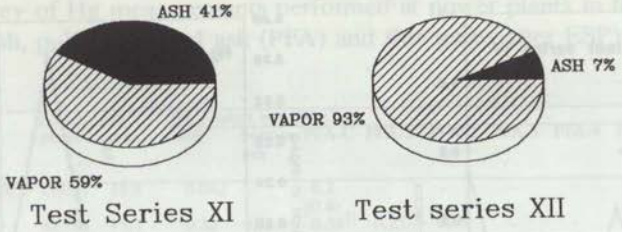

Fig. 3. The ratio Hg in ash (solid) and flue gases (vapor) in 600 MW(e) coal-fired power plants.

With respect to the original content in the coal the percentage of Hg in the vapor phase varies between 1 and 98% (mean 42±28%). A contribution of about 90% is expected, taking into consideration the high volatility of Hg. The question arises whether the measurements were performed accurately. A considerable amount of attention was paid to this subject. At the laboratory a calibration gas of Hg^0 was prepared followed by studies of adsorption on various materials and on the collection efficiency of impingers, wash-bottles and activated carbon (Meij and Sprong, 1982; Meij *et al.*, 1989; Meij, 1991). For three days the repeatability of the method with activated carbon was studied in practice in test series XIV: n=6, x=2.2 $\mu g \bullet m_o^3$, s=0.6 $\mu g \bullet m_o^3$ (v=27%). Furthermore, almost all measurements were performed in duplicate. In large tests more samples were taken. The next question is to what extent the coal sample matches the flue-gas sample. A considerable amount of attention was also paid to this subject.

A verification of the measurements is provided by the mass balances. Mass balances could be established for five tests (see Table III). The mass balances lie between 0.7 and 1.2. and in these cases between 57 and 91% of the Hg was found in the vapor phase (see also Fig. 3). It is concluded that the amount of Hg present in the flue gases after ESP is variable. There is no correlation found with the power station. Of the five tests four were performed at the Amer Power Station unit 8, which is equipped with tangential burners. One test (XII) was established at the Gelderland Power Station unit 13, which is wall-fired. A correlation is found with the concentration of HCl in the flue gases, see Fig. 4 (series XIV and XV). If the concentrations of HCl are relatively high (≈150 $mg \bullet m^{-3}$, coa of marine origin) the percentage of the total Hg content in the vapor phase is relatively low. In case of relatively low concentrations of HCl (≈25 $mg \bullet m^{-3}$, coal of fluviatile origin) the percentage of the total Hg in the vapor phase will be relatively high.

An explanation may be that Hg in the flue gases is initially in the elemental form. When relatively high concentrations of HCl are present some Hg is oxidized probably to $HgCl_2$. The oxidized Hg is predominantly present in the vapor phase at temperatures down to 140°C. At lower temperatures the oxidized Hg is in whole or in part adsorbed by fly ash. The temperatures of the flue gases in the ESP vary between 110 and 140°C. The amount

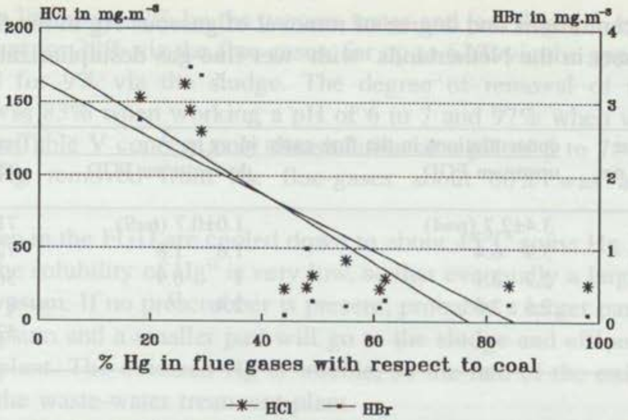

Fig. 4. The relation between the percentage gaseous Hg in the flue gases with respect to the Hg as original present in the coal with the amount of HCl and HBr.

of Hg in the vapor phase varies accordingly. This mechanism resembles the findings as described by Bergström in 1986 for waste incineration.

These results are also in generally agreement with the findings of the Swedish Coal-Health-Environmental project: 50% of the total quantity of Hg is separated by means of effective dust cleaning and 25 to 75% of the Hg emitted is soluble in water (KHM, 1983). Brosset (1987) carried out a detailed study of gaseous Hg in smoke from coal-fired power plants in Sweden. Three species of gaseous Hg were measured (in brackets the relative contribution to the total Hg present): Hg^0 (25 to 59%), and two forms of oxidized Hg (e.g. $HgCl_2$, 5 to 29%; e.g. $HgClCH_3$ 32 to 51%). Later on it appeared that no methylated form in flue gases exists, but that the third kind of species was probably Hg present in aerosols.

3.3 INFLUENCE OF FLUE-GAS DESULPHURIZATION

3.3.1. *Removal Of Gaseous Hg From The Flue Gases.* All FGDs in the Netherlands are based on the wet lime/limestone - gypsum process. The tests XII, XVc, XVd and XVh included measurements of gaseous Hg in the flue gases upstream and downstream of the FGD (Meij and Alderliesten, 1989). The results are given in Table IV. The extent of removal is between 8 and 72%, with an average of 52%. This average value is strongly influenced by the value of 8%, which deviates from the other values. The final concentrations in the flue gases, as emitted into the air, lie between 1 and 2 $\mu g \bullet m_o^{-3}$. This extent of removal is in agreement with the results of a similar study performed in West Germany (60%) (Gutberlet, 1984) and with the findings of the Swedish Coal-Health-Environment Programm (75%) (KHM, 1983).

A prescrubber was only present in test XII. Hence, leaving out a prescrubber does not

Table IV. Concentrations and degree of removal of gaseous Hg in the flue gases of coal-fired power plants in the Netherlands with wet flue-gas desulphurization plants

series	plant size MW(e) net	concentrations in the flue gases in $\mu g.m_o^{-3}$ upstream FGD	downstream FGD	removal in FGD (%)
XII	300	3.4±2.7 (n=4)	1.0±0.7 (n=9)	71
XVc	620	5.9 6.4	1.6 1.8	72
XVe	500	2.2 2.1	1 0.9	56
XVh	300	2.6 2.6	2.4 1)	8
average				52±30

1) sample lost

appear to affect the degree of Hg removal. A one-vessel process for the treatment of all flue gases of a 600 MW(e) plant was only applicable to the Amer power plant unit 8 (XVc). This one-vessel process does not have any negative influence on the removal of Hg.

3.3.2. A Mass Balance Study Of The FGD Plant. Test series XII lasted three days, during which all streams were sampled on each day (Meij and Alderliesten, 1989; Meij 1989). At that time only half of the flue gases were desulphurized. Hg is not only introduced by flue gases, but also by process water (river water), limestone and some lime for neutralisation of the effluent. Besides the flue gases, as discussed above, outgoing streams are gypsum, effluent and sludge from the waste water plant. The Hg concentrations, flows and relative contribution of all these streams are given in Table V (see also Fig. 5). A complication is that the Hg concentrations in the limestone and gypsum are below the limit of detection. However, the quantities of these two streams make that low concentrations might still be important. The mass balance studies were performed assuming concentrations on the detection limit level. The Hg mass balance for FGD is then about 0.85. Sixty six % was introduced by the flue gases, up to 33% could be

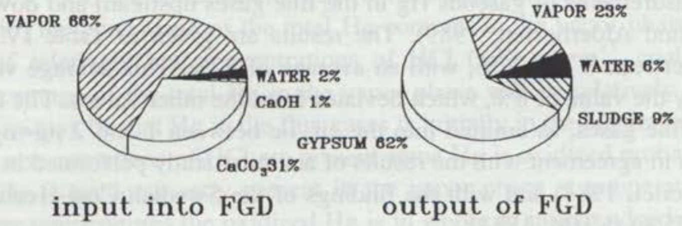

Fig. 5. The relative flow of Hg (expressed in %) in all ingoing and outgoing streams of the FGD.

introduced by the limestone, 2% by the process water and less than 1% by the lime. The Hg leaves the plant for 32% via the flue gases, for up to 62% via the gypsum, for 6% via the effluent and for 9% via the sludge. The degree of removal of the waste-water treatment plant was 83% when working a pH of 6 to 7 and 97% when working a pH of 11. The values in Table V concern only the situation at a pH of 6 to 7.

Of the total Hg removed from the flue-gases about 60% was absorbed in the prescrubber.

As the flue gases in the FGD are cooled down to about 45°C some Hg in the gas phase will condense. The solubility of Hg^0 is very low, so that eventually a large part of the Hg ends up in the gypsum. If no prescrubber is present, probably a larger part of the Hg will end up in the gypsum and a smaller part will go to the sludge and effluent of the waste-water treatment plant. The oxidized Hg is soluble, so the fate of the oxidised Hg is not the gypsum but the waste-water treatment plant.

Other measurements in the Netherlands indicated Hg concentrations in the gypsum of 0.6, <0.2 (EPON, 1988) and 1.2 $mg \cdot kg^{-1}$. Although the gypsum is an important route for the Hg in the FGD plant, the concentrations still remain very low.

Table V. Mass balances of Hg in the flue-gas desulphurization unit of a coal-fired power plant (series XII)

in				out				mass balance
process water	flue gases	lime-stone	lime	flue gases	gypsum	sludge	effluent	out/in
concentration in $mg \cdot kg^{-1}$ or $mg \cdot m^{-3}$:								
2	3.4	<0.5	<0.5	1	<0.5	6	8	
flows in $mg.h^{-1}$:								
93	2744	<1279	<40	807	<2199	316	227	≈0.85
relative contribution in %:								
2	66	<31	<1	23	<62	9	6	

3.4. ENVIRONMENTAL LOAD OF Hg FROM A COAL-FIRED POWER PLANT

The annual Hg emission by a 600 MW(e) power plant was reduced from 50 kg to less than 25 kg by introducing FGD. The emission factor is then about 0.5 $mg \cdot GJ^{-1}$ or 5 $\mu g \cdot kWhr^{-1}$. If atmospheric dispersion is taken into consideration, the maximum yearly average concentration at ground level is <4 $pg \cdot m^{-3}$. The background concentrations in the Netherlands are about 4 $ng \cdot m^{-3}$. Therefore the maximum increase of the ground level - concentration is limited to 0.1%.

Based on series XII (including FGD) each year an amount of about 2.5 kg Hg is released to the surface water. Via sludge and gypsum about 4 and 12 kg Hg are released, respectively. Nowadays the waste-water treatment plant is more efficient, releasing less Hg to the surface water and more via the sludge.

4. Conclusions

- The Hg concentrations in coal as imported by and fired in the Netherlands are low, the weighted average being about 0.2 mg•kg^{-1}. The lowest concentrations were found in coal from Australia and Colombia, the highest concentrations in coal from Poland.
- The variation in Hg concentrations within one lot of coal is small.
- Hg concentrations in ash, lime, limestone and gypsum are low (below 1 mg•kg^{-1}).
- The amount of Hg in the pulverized-fuel ash as collected in the ESP varies between 7 and 43%.
- A large part of the Hg in coal is emitted in the gas phase via the flue gases. An average concentration of 4.1 μg•m$_0^{-3}$ is found if no FGD is present. The Hg in the gas phase is 57 to 91% of the total Hg, based on complete mass balance studies and 1 to 98% (average 42%), based on measurements in coal and flue gases only. If the concentrations of HCl in the flue gases are relatively high (≈150 mg•m^{-3}, coal of marine origin) the amount of Hg measured in the vapor phase is low; if the concentrations of HCl are relatively low (≈25 mg•m^{-3}, coal of fluviatile origin) the amount of Hg in the vapor phase is high.
- The Hg in the gas phase is present in two chemical forms: elemental Hg and a less volatile form, probably $HgCl_2$.
- The Hg mass balances of five series performed at coal-fired power plants in the Netherlands lay between 0.7 and 1.2.
- By introducing wet FGD 50 to 70% of the Hg in the flue gases will be removed, leaving a residual concentration of 1 to 2 μg•m$_0^{-3}$.
- In FGD Hg also can be introduced by limestone (or lime).
- Hg leaves the FGD plant for 25% via the flue gases, for 60% via the gypsum, for 10% via the sludge and for 5% via the effluent of the waste-water treatment plant.

ACKNOWLEDGMENTS

We would like to thank the Dutch electricity generating companies for their cooperation. We are grateful for the support of the staff of the analytical laboratory of ECN.

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