

A study of trace element behaviour in two modern coal-fired power plants

II. Trace element balances in two plants equipped with semi-dry flue gas desulphurisation facilities

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Abstract

Two Finnish coal-fired power plants were experimentally investigated with regard to the distribution of environmentally harmful trace elements in the process. The plants were equipped with low NO_x burners, an electrostatic precipitator and a semi-dry flue gas desulphurisation unit consisting of a spray-dryer-type reactor and a fabric filter. All the in-going and out-going mass streams were analysed for As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se and Tl in the first plant, and for As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Tl and Zn in the other plant. Total atmospheric emissions of trace elements from the plants studied were very low; most of them even orders of magnitudes smaller than 10 µg/m³ (NTP). The vaporous fraction of the trace elements was found to play a predominant role in the atmospheric emissions. However, the total atmospheric emissions of even the strongly volatile Hg were very low, which can be ascribed to the applied plant technology. Enrichment of the elements into the various ash streams—from the bottom ash up to the particulates downstream of the electrostatic precipitator—was found to be in satisfactory compliance with literature data. Element balances were calculated over the whole process and over the desulphurisation unit for both plants: for the whole process the closure (i.e., ratio output/input) of element balances was within ±30% for all elements studied, except for chromium in plant HB, and for the vast majority of elements it was even within ±20%. The results imply that the

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sampling techniques and analytical methods developed for this work can be well applied to quantitative mass balance studies in this kind of processes. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Trace elements bound in coal are mobilised during coal combustion, and subsequently, released to the environment. Because they do not decompose in the environment, they may accumulate in food chains. If present in sufficient quantities, certain trace elements are very toxic. Therefore, they may pose a serious hazard to living organisms. Accordingly, it is necessary to reduce the emissions of potentially hazardous trace elements into the atmosphere. At the same time, it should be ensured that reducing emissions to the atmosphere does not cause increased pollution due to the formation of solid or liquid waste products.

The concern over trace element emissions is demonstrated in part by the USA's Clean Air Act Amendments law of 1990. The law defines 189 air toxics for which special abatement measures are required, and a lot of research has been focused on them. Trace metals As, Sb, Cd, Cr, Co, Pb, Mn, Hg and Ni belong to this list of 189 air toxics. As mentioned in the first part of this paper [1], the use of modern flue gas cleaning technique (e.g., flue gas desulphurisation and catalytic NO_x reduction) alters the partitioning of the elements between the flue gases and by-products. The overall optimisation of the operation of the plant requires an understanding of the partitioning of hazardous trace elements in the process. The partitioning can be characterised in terms of experimentally determined trace element balances over the whole process and over the sub-units. A reliable closure of trace element balances is required to evaluate quantitatively the impact of the chemical form, solubility, etc., of the trace elements in the emissions. This, in turn, is a prerequisite for the assessment of environmental impacts of the plant.

The element partitioning between different mass streams in coal-fired power plants has been studied by several authors [2–12]. During the last 10 years, research on power plant chemistry has included studies of element behaviour in modern flue gas cleaning systems such as a desulphurisation unit (FGD). A review of this kind of work has been presented by Clarke and Sloss [13].

The partitioning of trace elements between different mass streams during coal combustion has given rise to a classification into three (or more) element groups [2,3,6,7,13–17]. The classification demonstrates the different volatility of different elements. The term enrichment factor can be associated with different element groups. The enrichment factor illustrates the relative proportion of element contents in an output stream compared to that in the fuel stream. Enrichment factors have been discussed and used, e.g., by Maier et al. [5], Lim [16], Kaakinen et al. [2], Laitinen et al. [17] and Meij [6,7]. Meij has defined relative enrichment (RE) as follows:

$$RE = (C_{i,output} / C_{i,coal}) * [(\% \text{ ash})_{coal} / 100]$$

where *i* refers to element *i*. Elements can be classified according to the magnitude of the RE factor [6]:

Group	Relative enrichment (RE) according to Meij [6]	Characterisation of the elements in the group according to the review by Clarke and Sloss [13]
I	$0.7 < 1.3$ for all ashes	Elements concentrated in bottom ash, or partitioned equally between bottom ash and combustion fly ash
II	RE < 0.7 for bottom ash; RE \approx 1 for ESP* ash; RE > 1.3 for flu gas particles downstream of ESP	Elements concentrated more in the flue gas particles compared with bottom ash, especially enriched on the fine particles
III	RE < 1 for bottom ash and for ESP ash. Necessarily not enriched in flu particles	Elements volatilising most readily

* ESP = Electrostatic precipitator

The aim of our work was to characterise the behaviour of trace elements in two Finnish coal-fired power plants, and to compare the results with previous similar investigations. Our goal was also to provide tools, e.g., for the overall optimisation of the operation of the plant. The results of the work carried out to improve the quality of the sampling and analytical procedures for the plant measurements are presented in the first part of this article [1].

2. Scope of the investigation

The elements to be investigated were selected according to their abundance in typical flue gases of coal-fired power plants equipped with FGD as well as their environmental toxicity. The selected elements were As, Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn as well as more rarely investigated Se, Tl, Be and Co, which, however, were considered to have environmental relevance.

The actual measurement campaigns were preceded by two smaller field experiments. In these, the sampling techniques, sampling site, duration of the sampling period, the total mass of the grab samples, the number of the samples, storage and handling of the samples and analytical methods were evaluated for the final campaigns. The tentative content levels of the trace elements listed above were also determined.

The actual measurements at both plants (denoted as plant SB and plant HB hereinafter) were carried out as 2-week campaigns in two successive years. Trace element balances were determined for the plants. The results of four measurement days (i.e., four different tests) were selected to be used in final element balance calculations for plant SB, while the results of 6 days (i.e., six tests) were used in the calculations for plant HB.

The selection criteria for accepting results of different tests for element balance considerations were the stationary operation of the plant with maximum load during the sampling period.

3. Fuel and process description

The measurement campaigns were carried out in two power plants using pulverised Polish bituminous coal as fuel. The coal was characterised each day for its content of water, volatiles, ash and sulphur as well as for the higher and lower heat values. The average results are shown in Table 1. The ash content of the coal used in plant HB was remarkably higher and the heat value lower than those of the coal used in plant SB. This was due to the different quality of the coal in different years.

The maximum production capacity of the studied boiler of the plant SB is 160 MW of electricity plus 280 MW of district heating. For the boiler of the plant HB, the maximum capacity is 113 MW of electricity and 182 MW of district heating. During the measurements, the plants were operated at the full capacity in steady state conditions. In plant SB, the boiler is equipped with tangentially fired low- NO_x burners, while the boiler of plant HB has front-wall fired low- NO_x burners. The boilers were cleaned by soot blowers some hours before the measurements.

In plant HB, 99% and in plant SB over 99% of the particles are separated from the flue gases by an electrostatic precipitator (ESP). After the ESP, the flue gases of both plants are led to a semi-dry flue gas desulphurisation (FGD) unit consisting of a spray-dryer-type reactor and a fabric filter. Spray-dryer type refers to a process in which lime (CaO) is slaked with sea water (SB) or tap water (HB) and sprayed into the flue gas stream. The end-product of the flue gas desulphurisation consists mainly of a mixture of CaSO_3 , CaSO_4 and CaCl_2 . Water is evaporated during the reaction, so that no waste water is produced. The end-product of the FGD is separated from the flow by the fabric filter, which improves the collection efficiency by prolonging the reaction time of lime

Table 1

Analysis of coal from plants SB and HB (values on a dry basis)

		Plant SB	Plant HB
Moisture	wt. %	8.8	14.4
Volatiles	wt. %	29.4	29.6
Ash	%	11.8	22.6
HHV ^b	MJ/kg	30.7	25.2
LHV ^c	MJ/kg	29.7	24.3
C	wt. %	79.3	69–70 ^a
H	wt. %	5.2	4.4 ^a
N	wt. %	1.1	1.1–1.2 ^a
S	wt. %	0.9	1.1

^aAnalysis of coal shortly before the measurements.

^bHHV = higher heat value (calorimetric).

^cLHV = lower heat value (thermal).

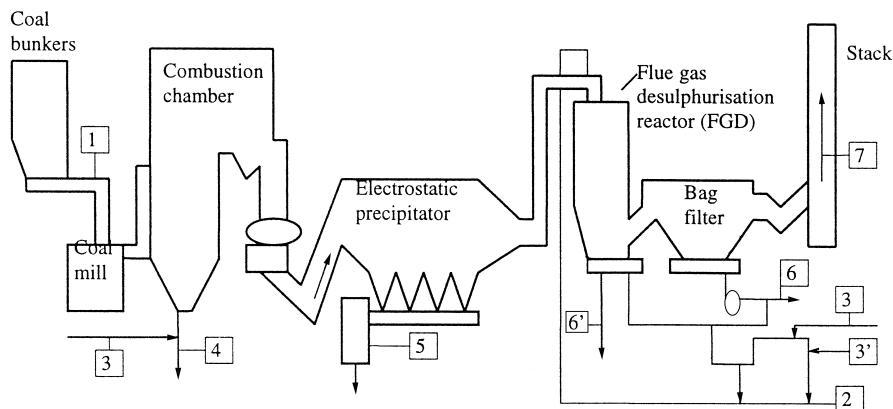


Fig. 1. A scheme of power plants SB and HB with electrostatic precipitators and spray-dryer-type flue gas desulphurisation. Incoming mass streams: 1, coal; 2, lime; 3, sea water; 3', raw water. Outgoing mass streams: 4, bottom ash; 5, ESP ash (ESP = electrostatic precipitator); 6, end product of FGD (FGD = flue gas desulphurisation); 6', coarse FGD product; 7, flue gas. Magnitudes of the mass streams are given in Table 3.

and SO_2 . A part of the end-product of FGD falls to the bottom of the reactor. This is circulated back to the spray in plant SB, whereas in the plant HB, it is separated from the circulation as a coarse fraction of FGD. A scheme of the plants and the mass streams considered in element balance determinations are shown in Fig. 1.

In addition to the element content in each mass stream, the flow rates of all the streams are necessary data for element balance calculations. The estimation of their magnitudes was done according to the information given by the plant operators. The flue gas flow rate was measured during each test.

Data on the operation of the plants during the measurements is given in Table 2. The magnitudes of the mass streams can be seen in Table 3a and b for plants SB and HB, respectively.

Table 2

Data on the operation of plants SB and HB during the measurement campaigns

		Plant SB	Plant HB
Fuel supply (dry)	t/h	62.8	58.4
SO_2 upstream the FGD	ppm	490	710
SO_2 downstream of FGD	ppm	91	95
SO_2 control	%	81	87
Flue gas flow rate ^a	$\text{m}^3/\text{h } 10^3$	638	495
Particles downstream of FGD ^b	mg/m^3	< 5	< 5
NO_x	ppm	270	210
O_2	%	5.5	6.8

^a Dry gas flow rate in the stack.

^b In dry flue gas, NTP (normal temperature and pressure: 0°C and 1 atm).

Table 3

Trace element contents in the mass streams, and magnitudes of mass streams of plants SB and HB

(a) Plant SB		Mass stream	Content	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
Coal	average	62.8 t/h	mg/kg ^a	4.1	1.3	0.18	8.8	29	23	0.08	92	31	18	0.9	< 0.5
	SD	0.45		0.1	0.2	0.06	1.5	3	1.2	0.01	10	3	1	0.2	—
Lime	average	1100 kg/h	mg/kg ^a	2.7	< 0.1	0.09	1.6	10	15	< 0.01	170	5.5	2.4	< 20	0.80
	SD	40		0.1	—	0.01	0.2	1	0.6	—	0.0	0.6	0.2	—	0.12
Sea water	average	16.7 m ³ /h	μg/l	< 4	0.08	0.17	< 0.8	0.53	1.7	< 1.0	7.1	< 0.7	4.5	2.1	2.2
	SD	0.8		—	0.03	0.04	—	0.10	0.8	—	1.2	—	0.6	0.6	0.7
Bottom ash	average	193 kg/h	mg/kg ^a	< 10	9.2	0.17	53	800	130	< 0.01	890	800	41	< 2.0	0.61
	SD	3		—	0.5	0.03	9	560	12	—	110	500	2	—	0.10
ESP ash	average	7550 kg/h	mg/kg ^a	39	13	1.5	70	200	184	0.31	820	250	170	5.6	3.1
	SD	58		2	1	0.6	7	16	2	0.04	50	10	20	1.3	0.3
Flue gas/ particulate	average		mg/kg ^a	170	18	7	140	440	420	5 ^c	740	430	540	190	26
	SD			32	5	2	27	220	120	—	200	91	120	40	11
upstream of FGD	average	631 * 10m ³ /h	μg/m ^{3b}	3.5	0.36	0.15	2.9	9.0	8.6	0.06	15	8.7	11	4	0.53
	SD	6 * 10 ³		0.7	0.10	0.05	0.6	4.4	2.5	0.06	4	1.9	2	3	0.22
Flue gas/ gaseous upstream of FGD	average	631 * 10m ³ /h	μg/m ^{3b}	1.6	0.49	0.4	0.89	2.4	3.4	4.1	64	1.5	1.5	13	2.2
	SD	6 * 10 ³		0.6	0.09	0.4	0.12	1.1	0.7	0.3	37	0.1	0.5	1	1.1
FGD product	average	2030 kg/h	mg/kg ^a	2.5	< 0.1	0.09	1.5	6.7	11	0.18	83	2.8	3.8	< 20	0.35
	SD	75		0.2	—	0.01	0.1	0.9	1	0.06	5	1.5	0.3	—	0.09
Flue gas/ particulate downstream of FGD	average		mg/kg ^a	17	< 0.1	1.1	< 11	160	360	14 ^c	960	280	6	< 7	< 12
	SD			14	—	0.5	—	83	230	—	590	150	4	—	—
upstream of FGD	average	638 * 10m ³ /h	μg/m ^{3b}	0.08	< 0.003	0.005	< 0.05	0.68	1.6	0.082 ^c	4.9	1.2	0.03	< 0.03	< 0.05
	SD	5 * 10 ³		0.06	—	0.002	—	0.36	1.0	—	2.2	0.6	0.02	—	—
Flue gas/ gaseous downstream of FGD	average	638 * 10m ³ /h	μg/m ^{3b}	< 2.5	< 0.98	0.5	< 2.2	6.3	11	1.8	6.7	2.4	3.3	< 9.0	< 2.3
	SD	5 * 10 ³		0.1	0.06	0.3	0.2	2.5	7	0.6	0.5	0.4	1.7	0.9	0.2

Table 3 (continued)

(b) Plant HB		Mass stream	Content	As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn
Coal	average	58.4 t/h	mg/kg ^a	6.3	3.0	0.23	39	0.15	190	26	33	0.9	69
	SD	2.3		0.8	0.4	0.02	1	0.05	13	2	6	0.3	9
Lime	average	1300 kg/h	mg/kg ^a	1.0	< 0.4	0.11	6.1	0.03	190	3.8	2.1	0.28	9.8
	SD	—		0.3	—	0.05	0.3	0.01	5	2	0.2	0.03	1.6
Sea water	average	12 m ³ /h	μg/l	< 5	< 5	< 0.5	4	< 0.1	25	3.4	< 5	< 6	< 0.01
	SD	—		—	—	—	4	—	4	3.1	—	—	—
Tap water	average	5 m ³ /h	μg/l	< 5	< 5	< 0.2	< 2	< 0.1	3	< 2	< 5	< 5	< 0.01
	SD	—		—	—	—	—	—	0.5	—	—	—	—
Bottom ash	average	1130 kg/h	mg/kg ^a	5.2	11	0.14	1000	0.26	940	800	53	0.9	123
	SD	87		0.8	1	0.04	400	0.13	50	170	6	0.2	5
ESP ash	average	10 200 kg/h	mg/kg ^a	32	14	1.1	150	0.38	790	71	190	4.8	330
	SD	800		2	1	0.1	11	0.05	20	4	20	0.6	52
Flue gas/ particulate/ upstream	average		mg/kg ^a	190	13	4.1	230	0.7 ^c	970	250	630	< 230	1000
	SD			81	2	1.0	45	—	120	350	120	—	260
of FGD	average	495 * 10 ³ m ³ /h	μg/m ³	46	3.5	1.1	70	0.19	270	25	170	< 16	280
	SD	17 * 10 ³		14	1.2	0.4	30	0.09	110	17	70	—	90
Flue gas/ gaseous upstream of FGD	average	495 * 10 ³ m ³ /h	μg/m ³	< 1.7	< 0.8	0.08	< 2.3	2.3	< 0.2	< 1.1	< 1.7	< 1.7	11
	SD	17 * 10 ³		—	—	0.07	—	0.8	—	—	—	—	4
Coarse FGD product	average	520 kg/h	mg/kg ^a	3.7	0.65	0.17	5.9	0.13	110	6.9	13	10.5	29
	SD	—		0.4	0.06	0.04	0.8	0.05	5	1	3	0.1	5
FGD product	average	4680 kg/h	mg/kg ^a	5.6	0.63	0.20	5.8	0.18	110	6.4	17	0.73	35
	SD	—		1.6	0.05	0.01	2.4	0.04	5	1	2	0.04	2
Flue gas/ particulate downstream of FGD	average		mg/kg ^b	< 26	< 8	< 2.3 ^d	60	0.17	130	< 4	12	< 16	370
	SD			—	—	—	100	0.01	56	—	10	—	300
Flue gas/ gaseous downstream of FGD	average	495 * 10 ³ m ³ /h	μg/m ³	0.13	< 0.04	< 0.01	0.12	0.0015	0.4	< 0.02	0.03	< 0.08	0.7
	SD	17 * 10 ³		—	—	—	0.10	0.0003	0.2	—	0.03	—	0.7
Flue gas/ gaseous downstream of FGD	average	495 * 10 ³ m ³ /h	μg/m ³	< 1.9	< 0.9	0.07	< 2.4	0.11	0.20	< 1.2	< 2.2	< 1.9	52
	SD	17 * 10 ³		—	—	0.02	—	0.01	0.06	—	—	—	23

4. Sampling

4.1. Flue gas sampling

The concentrations of O_2 , CO_2 , CO , SO_2 , NO_x in the flue gases were monitored continuously during the whole measurement campaigns. Particle concentration and flue gas flow rate were determined twice during each test.

Trace element samples from the flue gases were taken simultaneously upstream and downstream of the FGD plant. The sampling time was approximately 6 h. The sampling train for the simultaneous collection of both the particulate and the gaseous fraction of the elements was made entirely of glass or Teflon[®]. In plant SB, two parallel sampling trains were used on both measurement levels.

Particulate trace elements were collected on a filter. In plant SB, plane filters made of Teflon[®] (Fluoropore[®], pore 0.5 μm) were used on both measurement levels. In plant HB, the particles were collected on a thimble filter made of quartz fibre (Munktel MK360) upstream of the FGD, and on a plane Teflon[®] filter downstream of the FGD. The nozzle of the sampling probe was chosen to enable isokinetic sampling. After particle removal, the sample gas was conducted via the probe to the out-stack division, where the sample gas was divided into two sample streams of 1–2 l/min. One of the streams was conducted to a series of absorption bottles containing a solution of 4 wt.% $K_2Cr_2O_7$ /20 wt.% HNO_3 [18] for the collection of gaseous mercury (Hg), and the other stream to the absorption bottles containing 38 wt.% HNO_3 for the collection of other gaseous elements.

In order to clarify the terminology and concepts used in this paper, it is worth focusing attention on the following definitions: the fraction of flue gases collected on the sampling filter is called the particulate fraction, although it is possible that part of the vaporous fraction is adsorbed on particles collected on the filter. The fraction which penetrates the filter and is collected by the acidic absorption liquid is called the gaseous fraction in this paper, although it is possible that it contains a fraction of the smallest particles as well.

4.2. Sampling of other mass streams

The sampling of other mass streams (coal, bottom ash, ESP ash, lime, FGD products, water) was done by the staff of the plant. Based on previous sampling practice of the staff, a satisfactory sampling programme was developed. Samples were obtained as composites of grab samples taken at regular intervals over the period when the flue gases were being sampled.

Notes to Table 3:

^aOn dry-weight basis.

^bIn dry flue gas, NTP (normal temperature and pressure: 0°C and 1 atm).

^cResult of one measurement with extended duration.

^dOnly one result available.

—: Not possible to calculate the standard deviation.

Coal was sampled at hourly intervals during transport from the suppliers bringing coal to the mills. A mechanical sampling device was used. The total amount of coal collected was 200 kg during one test.

Grab samples of the boiler's bottom ash were taken from the front end of the slag conveyor downstream of the quenching basin. Samples of fly ash precipitated by the ESP (ESP ash) were taken separately each hour from an intermediate reservoir, to which the ash from all the fields were compiled (a total of 10 l/day).

Lime was sampled during a 3-h quenching period (a total of 2 kg). Samples of the end-product from flue gas desulphurisation (FGD product) were collected from the transmitter of the fabric filters at intervals of about 1 h (a total of 5 l/day). In plant HB, samples of the coarse fraction of the FGD product (coarse FGD product) were collected from the pre-separator of the by-product.

Two 1-l samples of the sea water and tap water used in the spray-dryer and in the quenching basin of the bottom ash were taken once per test.

4.3. Analysis of the samples

Gross samples of coal were first ground to a grain size of less than 5 mm. Then the samples were dried in air. Laboratory samples of 3–5 kg were taken from this gross sample. The laboratory samples were ground to a grain size of less than 0.1 mm before dividing them into smaller samples. Samples of bottom ash were dried and homogenised by means of grinding to a grain size of 0.1 mm. The division of solid samples into smaller ones was done by means of the manual 'cone to squares' method.

The techniques used in the digestion of solid samples and in the determination of trace element content were discussed in the first part of this work [1]. Flue gas particle samples collected on quartz fibre filters were digested according to the procedure described in Ref. [19].

In addition to common quality control checks (determination of method blanks, etc.), commercial reference materials were added to the digestion batch of each solid material. For the sake of improved quality assurance, two independent laboratories contributed to the analyses. A few samples of each sample type were digested in parallel by both laboratories, and the resulting two solutions were also analysed by both laboratories. This made it easier to recognise possible sources of error in the case of large deviations or other uncertainties.

5. Results

5.1. Element contents

Trace element contents in different solid mass streams calculated on a dry weight basis, as well as element concentrations in the flue gases and process waters, are given as mean values together with the standard deviations (SD) in Table 3a and b. The values are based on the results of four different measuring days (tests) for plant SB and of 6 days (tests) for plant HB; the most striking outliers have been omitted.

Table 4

Relative enrichment factors (RE) for different trace elements calculated according to the definition presented by Meij [6,7] in plants SB and HB

(a) Plant SB		As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
Bottom ash	average	0.1	0.8	0.1	0.7	3.4	0.7	0.01	1.1	3.1	0.3	0.1	n.c. ^a
	SD	0.002	0.1	0.02	0.3	2.2	0.06	0.001	0.08	2.1	0.02	0.05	—
ESP ash	average	1.1	1.1	1.0	1.0	0.8	0.9	0.5	1.1	0.9	1.1	0.8	n.c. ^a
	SD	0.06	0.1	0.1	0.1	0.09	0.02	0.13	0.14	0.06	0.06	0.2	—
Particles upstream of FGD	average	4.4	1.6	4.6	2.1	2.6	2.3	6.1 ^c	1.1	1.8	3.8	5.8	n.c. ^a
	SD	0.7	0.2	0.8	0.5	0.4	0.8	—	0.3	0.3	0.8	2.2	—
FGD product	average	0.07	0.005	0.07	0.02	0.028	0.055	0.3	0.11	0.01	0.02	1.4	n.c. ^a
	SD	0.01	0.001	0.01	0.004	0.002	0.003	0.1	0.01	0.01	0.002	0.5	—
Particles downstream of FGD	average	1.1	n.c. ^b	1.3	n.c. ^b	0.7	1.9	19 ^c	1.5	1.1	0.05	n.c. ^b	n.c. ^a
	SD	0.9	—	0.7	—	0.2	0.7	—	0.5	0.5	0.03	—	—
(b) Plant HB		As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn		
Bottom ash	average	0.2	0.7	0.1	5.1	0.3	1.0	5.0	0.3	0.2	0.4		
	SD	0.03	0.03	0.04	1.7	0.1	0.1	1.3	0.04	0.06	0.04		
ESP ash	average	1.0	0.9	0.9	0.7	0.5	0.8	0.5	1.1	1.1	0.9		
	SD	0.2	0.04	0.2	0.06	0.15	0.01	0.05	0.13	0.3	0.14		
Particles upstream of FGD	average	6.1	0.8	3.5	1.1	1.0	1.0	2.0	3.7	n.c.	3.0		
	SD	3.4	0.08	1.2	0.2	0.4	0.1	2.8	0.6	—	0.9		
Coarse FGD product	average	0.1	0.04	0.1	0.03	0.2	0.1	0.1	0.1	0.1	0.1		
	SD	0.03	0.003	0.02	0.005	0.1	0.003	0.008	0.02	0.04	0.018		
FGD product	average	0.2	0.04	0.2	0.03	0.3	0.1	0.05	0.1	0.2	0.1		
	SD	0.04	0.004	0.02	0.01	0.1	0.005	0.01	0.02	0.04	0.01		
Particles downstream of FGD	average	n.c. ^b	n.c. ^b	2.1 ^d	0.3	0.2 ^d	0.1	n.c. ^b	0.08	n.c.	1.0		
	SD	—	—	—	0.50	—	0.05	—	0.07	—	0.9		

^a n.c.: Not calculated, because the content in coal was below the limit of determination.^b n.c.: Not calculated, because the content in the ash was below the limit of determination.^c Result of one measurement with extended duration.^d Only one result available.

—: Not possible to calculate the standard deviation.

The contents in the mass streams entering the process indicate that the coal used in plant SB is richer than lime in As, Be, Cd, Co, Cr, Cu, Hg, Ni and Pb, while the content of Mn and Tl is higher in lime. For Se, the low content combined with the high detection limit of the analysis did not make this kind of comparison possible. In the case of plant HB, the coal is richer than lime in As, Be, Cd, Cr, Hg, Ni, Pb, Tl and Zn, while the content of Mn in coal and lime are approximately equal. The element contents in coal are in each case inside the content ranges reported in the literature [4,13,17].

Considering the solid mass streams leaving the plant, it can be seen that the contents of As, Be, Cd, Co, Cu, Hg, Pb, Se and Tl in plant SB and the contents of As, Be, Cd, Hg, Pb, Tl and Zn in plant HB are highest in ESP ash, while bottom ash is richer than any other ash in Cr, Mn and Ni in both plants. One of the most striking observations is the high content of Hg in bottom ash in plant HB together with the relatively high Hg contents also in ESP ash and in FGD product. In plant SB, such high contents in bottom ash were not observed, although the contents in ESP ash and in FGD product were of the same order of magnitude than in plant HB.

The concentrations of gaseous Be, Cd, Hg, Mn, Se and Tl in the flue gas in plant SB and that of gaseous Hg in plant HB upstream of the flue gas desulphurisation (FGD) exceed the corresponding particulate concentrations. For all of the other elements, the concentrations in the particulate phase are predominant upstream of FGD.

Downstream of FGD, i.e. in the stream emitted into the atmosphere, the element concentrations in the flue gases are, in general, very low. The predominant role of the gaseous fraction of the elements downstream of FGD is evident on the basis of the results from plant SB. In plant HB, the concentrations of the elements downstream of FGD were mostly below the determination limits of the analytical methods applied. For Cd, Hg, and Zn, it was possible to determine the concentrations in the gaseous phase to be higher than in the particulate phase. For Mn, the opposite was observed. It is worth noticing that the concentration of Hg in the atmospheric emissions from plant HB was lower than from plant SB, and considerably lower than expected on the basis of data presented in the literature.

Table 4 shows the relative enrichment of metals in the various ash streams after combustion, calculated according to the definition presented by Meij [6]. No enrichment was found for Mn, which is characteristic of elements belonging to group I. Enrichment of As, Cd, Co, Cu and Pb into the flue gas particles upstream of the FGD was observed. Consequently, these elements fall into the group II. In plant SB, Hg and Se are strongly enriched in the fly ash particles and fall rather into group II than into group III. This is true for Hg also in plant HB. Be shows behaviour between groups I and II. No enrichment of the elements classified into group II was observed downstream of the FGD.

The high enrichment factors of Cr and Ni in the bottom ash are not consistent with literature data. The high standard deviations of the Cr and Ni contents especially in bottom ash (see Table 3a and b) indicated some difficulties associated with the determination of these metals. The difficulties may be caused by contamination due to the construction materials used in the plant or by analytical problems. However, because the mass balance closures for Cr and Ni (see below) could generally be considered satisfactory, the results for these elements were included in the calculations.

Table 5

Trace element balances over the whole process of plants SB and HB

(a) Plant SB		As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
Coal	average mg/h	238 000	76 000	10 000	507 000	1 650 000	1 350 000	4700	5 320 000	1 780 000	1 060 000	52 000	< 29 000
	SD	77 000	9800	3400	81 000	200 000	72 000	760	610 000	140 000	77 000	12 000	—
Lime	average mg/h	2800	< 140	96	1700	10 000	15 000	< 10	180 000	5800	2500	< 20 000	850
	SD	120	—	12	280	1600	900	—	7000	740	310	—	160
Sea water	average mg/h	< 90	1.3	2.9	< 20	8.8	28	< 20	120	< 20	75	35	23
	SD	—	0.4	1.0	—	2.0	14	—	13	—	17	9	10
Total input	g/h	240	76	10	510	1700	1400	4.7	5500	1800	1100	n.c.	n.c.
Maximum uncertainty	g/h	77	10	3	81	200	73	0.8	620	140	77	n.c.	n.c.
Bottom ash	average mg/h	< 2000	1800	32	10 000	160 000	25 000	< 5	170 000	150 000	7900	< 390	120
	SD	—	98	6	1800	110 000	2300	—	22 000	96 000	400	—	19
ESP ash	average mg/h	300 000	96 000	12 000	530 000	1 500 000	1 390 000	2300	6 200 000	190 000	1 320 000	43 000	24 000
	SD	140 000	7000	4700	54 000	130 000	15 000	320	370 000	85 000	140 000	9700	2000
FGD product	average mg/h	4900	< 200	190	2900	13 000	22 000	430	170 000	4000	7700	< 40 000	710
	SD	550	—	33	180	1500	1800	34	15 000	180	800	—	190
Flue gas/particulate	average mg/h	55	< 1.7	3.0	< 35	440	1000	52	3100	780	17	< 18	< 35
	SD	39	—	1.5	—	83	490	10	1400	400	12	—	—
Flue gas/gaseous	average mg/h	< 1700	< 700	290	< 1400	5600	7300	1300	4300	1500	2100	< 5900	< 1400
	SD	—	—	200	—	4600	4700	260	330	270	1100	—	—
Total output	g/h	300	98	12	550	1700	1400	4.1	6500	2000	1300	n.c.	24
Maximum uncertainty	g/h	141	7	5	56	246	24	0.6	409	182	142	n.c.	2
Output/input		1.25	1.28	1.18	1.08	1.00	1.00	0.88	1.18	1.11	1.18	n.c.	n.c.
Maximum uncertainty		0.99	0.26	0.88	0.28	0.26	0.07	0.28	0.21	0.19	0.21	n.c.	n.c.

Table 5 (continued)

(b) Plant HB			As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn
Coal	average	mg/h	313 000	150 000	11 600	196 000	7300	9 500 000	1 290 000	1 660 000	47 000	3 400 000
	SD		39 000	23 000	1300	82 000	2600	820 000	200 000	340 000	16 000	520 000
Lime	average	mg/h	1300	< 520	140	7900	22	250 000	5000	2800	360	13 000
	SD		450	—	60	360	16	6700	2000	250	33	2100
Sea water	average	mg/h	< 37	< 37	< 4	26	< 0.74	180	25	< 37	< 37	< 0.07
	SD		—	—	—	26	—	32	23	—	—	—
Raw water	average	mg/h	< 25	< 25	< 1	< 10	< 1	15	< 10	< 25	< 25	< 0.1
	SD		—	—	—	—	—	2.5	—	—	—	—
Total input		g/h	310	150	12	2000	7.3	9800	1300	1700	47	3500
Maximum uncertainty		g/h	39	23	1	82	3	830	200	340	16	520
Bottom ash	average	mg/h	5800	12 000	150	1 160 000	300	1 100 000	890 000	60 000	970	140 000
	SD		550	1700	50	340 000	170	34 000	120 000	9800	210	13 000
ESP ash	average	mg/h	320 000	140 000	11 000	1 520 000	3900	8 000 000	730 000	1 900 000	49 000	3 400 000
	SD		34 000	19 000	2000	100 000	670	610 000	75 000	340 000	10 000	770 000
Coarse FGD product	average	mg/h	1900	250	87	3100	68	55 000	3600	6600	280	15 000
	SD		220	67	18	390	27	2700	600	1400	63	2600
FGD product	average	mg/h	26 000	2900	940	27 000	820	490 000	30 000	80 000	3400	160 000
	SD		7300	260	55	11 000	190	26 000	5000	8900	170	11 000
Flue gas/particulate	average	mg/h	< 65	< 20	< 2	58	< 1	200	< 10	16	< 40	330
	SD		—	—	—	49	—	95	—	15	—	190
Flue gas/gaseous	average	mg/h	< 920	< 430	36	< 1200	38	93	< 620	< 1000	< 900	25 000
	SD		—	—	7.3	—	17	27	—	—	—	10 000
Total output		g/h	350	160	12	2700	5.1	9700	1700	2000	54	3700
Maximum uncertainty		g/h	42	21	2	450	1.1	670	200	360	10	810
Output/input			1.13	1.06	1.06	1.35	0.70	0.99	1.28	1.18	1.15	1.06
Maximum uncertainty			0.28	0.30	0.31	0.28	0.41	0.15	0.35	0.45	0.61	0.39

n.c.: Not possible to estimate because the contents in important mass streams were below the determination limit.

—: Not possible to calculate the standard deviation.

5.2. Element balances over the whole plant

The element balances over the whole process are given in Table 5a and b. Element flows in different mass streams are presented as means together with the standard deviations. The maximum uncertainty of the total input and output of each element has been estimated on the basis of the standard deviations for each element stream. The fractions of trace elements (of the total input) entrained to mass streams other than flue gases were calculated for the situations upstream and downstream of the FGD. These results are given in Table 6a and b.

As an indicator of the accuracy of the overall measurement, the mass balance closures (i.e., ratio output/input) together with estimates for the maximum uncertainty of this ratio for different elements in both plants are shown in Table 5a and b. The estimate for the maximum uncertainty of the closure has been calculated on the basis of the uncertainty estimates for the total output and input streams. The closures are relatively close to 100%, varying from 88% for Hg to 128% for Be in plant SB. In plant HB, the closures vary from 70% for Hg to 135% for Cr. Negative balances observed in both plants for Hg indicate the complexity of reliable sampling of Hg especially in flue gas.

As expected, coal itself is by far the main source of trace elements entering the plant. In general, it was observed that only a few percent of trace elements investigated enter the plant in lime. This percentage was highest for Mn (3.4%) in plant SB, and for Mn (2.7%) in plant HB. Sea water and tap water can be regarded as almost negligible sources of trace elements entering the plant.

When considering the output streams of the trace elements, it can be seen that in plant SB the ESP ash is the predominant route for the elements leaving the plant. Bottom ash is the second most important for Be, Co, Cr and Ni, while end-product of FGD is the second most important for As, Cd, Hg and Tl. In the case of Cu, Mn and Pb, the differences between the magnitudes of the element flows contained in FGD product and in bottom ash were not significant.

The role of ESP ash as a discharge route for trace elements in plant HB is the most important, but not as pronounced as in plant SB because of the lower collection efficiency of the ESP in plant HB. Bottom ash plays a more significant role in plant HB than in plant SB. More Be, Cr, Mn and Ni leaves plant HB in the bottom ash than in the FGD product, while more As, Cd, Hg and Tl leaves plant HB in the FGD product than in the bottom ash. Also, somewhat higher amounts of Pb and Zn, leave the plant in the FGD product than in bottom ash. The amount of Ni leaving the plant in bottom ash exceeds the amount of Ni leaving the plant in ESP ash. This may, however, be due to possible analytical or contamination problems, as discussed above.

As for the output streams of Hg, a much higher amount of Hg is found in the solid mass streams in plant HB than in plant SB. For instance, no Hg was detected in bottom ash in plant SB, while approximately 6% of Hg leaving plant HB was found in this mass stream.

The mass stream studies show that a high proportion of the trace elements introduced to the plant are emitted from the plant in the solid mass streams. Considering the situation in the flue gas upstream of the FGD in plant HB, more than 80% of all trace

Table 6

Fraction of the amount of different elements entrained to other mass streams than to flue gas, % of the total input

(a) Plant SB	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
<i>Upstream of FGD / total input, %</i>												
Particulate	> 99	> 99	> 99	> 99	> 99	> 99	99	> 99	> 99	> 99	96	n.c
Total (particulate + gaseous)	99	> 99	97	> 99	> 99	> 99	47	> 99	> 99	> 99	80	n.c
<i>Downstream of FGD / total input, %</i>												
Particulate	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99	> 99.9	> 99.9	> 99.9	> 99.9	n.c
Total (particulate + gaseous)	> 99	> 99	97	> 99	> 99	> 99	71	> 99.9	> 99.9	> 99	> 89	n.c
(b) Plant HB	As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn		
<i>Upstream of FGD / total input, %</i>												
Particulates	92	99	95	98	99	98	> 99	94	> 83	96		
Total (particulate + gaseous)	< 92	> 98	94	> 98	83	> 98	> 99	> 94	> 81	95		
<i>Downstream of FGD / total input, %</i>												
Particulates	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9	> 99.9		
Total (particulate + gaseous)	> 99.7	> 99.7	> 99.7	> 99.9	99.5	> 99.9	> 99.9	> 99.9	> 98	99.3		

n.c.: Not calculated, because relevant concentrations were below the limit of determination.

Table 7
Trace element balances over the flue gas desulphurisation unit (FGD) of plants SB and HB

(a) FGD of plant SB			As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
Lime	average	mg/h	2800	< 140	96	1700	10 000	15 000	< 10	180 000	5800	2500	< 20 000	850
	SD		120	—	12	280	1600	900	—	7000	740	310	—	160
Sea water	average	mg/h	< 40	0.8	1.9	< 8	5.6	18	< 10	74	< 7	48	22	17
	SD		—	0.3	0.6	—	1.2	8.8	—	7.9	—	11	5.7	6.0
Flue gas/particulate upstream of FGD	average	mg/h	2200	230	93	1800	5700	5500	52	9500	5500	6900	2000	340
	SD		420	60	32	360	2800	1600	29	2600	1200	1600	1800	140
Flue gas/gaseous upstream of FGD	average	mg/h	1000	310	240	560	1500	3200	2400	41 000	930	930	8300	1400
	SD		370	57	280	80	680	2400	430	24 000	80	330	720	710
Total input		g/h	6.0	0.54	0.43	4.1	17	24	2.5	230	12	10	n.c.	2.6
Maximum uncertainty		g/h	0.9	0.12	0.32	0.7	5.1	4.9	0.5	34	2.0	2.3	n.c.	1.0
FGD product	average	mg/h	4900	< 200	190	2900	13 000	22 000	430	167 000	4000	7700	< 40 000	710
	SD		550	—	33	180	1500	1800	34	15 000	180	800	—	190
Flue gas/particulate downstream of FGD	average	mg/h	55	< 1.7	3.0	< 35	440	1000	52	3100	780	17	< 18	< 35
	SD		39	—	1.5	—	83	490	10	1400	400	12	—	—
Flue gas/gaseous downstream of FGD	average	mg/h	< 1700	< 700	290	< 1400	5600	7300	1300	4300	1500	2100	< 5900	< 1400
	SD		—	—	200	—	4600	4700	260	330	270	1100	—	—
Total output		g/h	5.0	n.c.	0.48	2.9	19	30	1.8	170	6.3	9.8	n.c.	n.c.
Maximum uncertainty		g/h	0.6	n.c.	0.23	0.2	6	7	0.3	17	0.9	1.9	n.c.	n.c.
Output/input			0.83	n.c.	1.12	0.71	1.12	1.25	0.71	0.74	0.52	0.94	n.c.	n.c.
Maximum uncertainty			0.22	n.c.	1.39	0.17	0.69	0.55	0.25	0.18	0.15	0.39	n.c.	n.c.

Table 7 (continued)

(b) FGD of plant HB			As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn
Lime	average	mg/h	1300	< 520	140	7900	22	250 000	5000	2800	360	13 000
	SD		450	—	60	360	16	6700	2000	250	33	2100
Raw water	average	mg/h	< 25	< 25	< 1	< 10	< 1	15	< 10	< 25	< 25	< 0.1
	SD		—	—	—	—	—	2.5	—	—	—	—
Sea water	average	mg/h	< 50	< 50	< 5	35	< 1.0	250	34	< 50	< 50	< 01
	SD		—	—	—	35	—	43	31	—	—	—
Flue gas/particulate upstream of FGD	average	mg/h	25 000	2000	610	37 000	100	150 000	11 000	98 000	< 8000	150 000
	SD		5400	190	120	8000	43	30 000	4300	22 000	—	16 000
Flue gas/gaseous upstream of FGD	average	mg/h	< 820	< 400	42	< 1200	1200	< 100	< 600	< 900	< 800	5500
	SD		—	—	29	—	400	—	—	—	—	1800
Total input		g/h	26	2.0	0.79	45	1.3	400	16	100	n.c.	170
Maximum uncertainty		g/h	6	0.2	0.2	8	0.5	37	6	22	n.c.	20
Coarse FGD product	average	mg/h	1900	250	90	3100	68	55 000	3600	6600	280	15 000
	SD		220	67	18	390	27	2700	600	1400	63	2600
FGD product	average	mg/h	26 000	2900	940	27 000	820	490 000	30 000	80 000	3400	160 000
	Sd		7300	260	55	11 000	190	26 000	5000	8900	170	11 000
Flue gas/particulate downstream of FGD	average	mg/h	< 65	< 20	< 2	58	< 1	190	< 10	16	< 40	330
	SD		—	—	—	49	—	95	—	15	—	190
Flue gas/gaseous downstream of FGD	average	mg/h	< 920	≪ 450	36	< 1200	38	93	< 620	< 1100	< 930	25 000
	SD		—	—	7.3	—	17	27	—	—	—	10 000
Total output		g/h	28	3.2	1.1	30	1	550	34	87	3.7	200
Maximum uncertainty		g/h	8	0.3	0.1	11	0.2	29	6	10	0.1	24
Output/input			1.08	1.60	1.35	0.67	0.72	1.38	2.13	0.87	n.c.	1.18
Maximum uncertainty			0.53	0.32	0.45	0.38	0.44	0.20	1.19	0.29	n.c.	0.28

n.c.: Not possible to estimate because the contents in important mass streams were below the determination limit.

—: Not possible to calculate the standard deviation.

elements had already been distributed to mass streams other than flue gases. As for the situation in the flue gas downstream of the FGD, even 98% of the trace elements introduced into the plant in fuel and lime had been distributed to solid mass streams, due to the entrainment of trace metals to the by-product of the desulphurisation process. The same tendency was also found in plant SB, with the exception of Hg. Only 47% of Hg was in ash streams other than the flue gases by the time the flue gases had reached the FGD, and 71% downstream of the FGD.

5.3. Element balances over the FGD plant

The element balances over the FGD unit are shown in Table 7a and b. Element flows are given as mean values together with the standard deviations in Table 7a for plant SB (four measurement days) and in Table 7b for plant HB (six measurement days). The estimations of uncertainties for the total output and input were carried out in the same way as those shown in Table 5a and b. The element contents in the mass streams entering and leaving the FGD were generally closer to the limits of determination of the analytical techniques than in the case of the whole plant. Therefore, there is more uncertainty in the results for the FGD plant.

The accuracy of the element flow measurement is characterised by means of the element balance closures (ratio output/input) of different elements over the FGD unit shown also in Table 7a and b. The estimations of the maximum uncertainties for the mass balance closure were carried out in the same way as in the case of the whole plant (see Table 5a and b). The values vary from 52% for Ni to 125% for Cu in plant SB, and from 67% for Cr to 186% for Ni in plant SB. These values are much poorer than the values obtained for the whole process. Also, the estimated uncertainties in the value of the mass balance closure (output/input ratio) are higher than those for the whole process. This can be explained by the difficulty in measuring low element contents after the FGD and by the uncertainty of measuring the mass streams due to the recirculation of part of the lime in plant SB.

The collection efficiencies of the FGD unit for different elements are shown in Table 8. Considering the collection efficiency of FGD for particulate metals, an efficiency higher than 90% is found for all those elements, for which the calculation could be done. However, when the gaseous phases of the elements are included in the evaluation, much lower total collection efficiencies of metals were observed. For instance in plant SB, the collection efficiency for Cd was 32%, for Hg 44%, for Cu 65%, Cr 65% and for Ni

Table 8
Collection efficiency of the flue gas desulphurisation unit (FGD), %

(a) FGD of plant SB	As	Be	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Se	Tl
Particulates	99	> 99	98	> 99	97	95	> 99.9	98	93	> 99.9	n.c.	> 97
Total (particulate + gaseous)	> 71	n.c.	32	> 65	65	65	44	97	81	79	n.c.	n.c.
(b) FGD of plant HB	As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Tl	Zn		
Particulates	> 99	> 99	> 99	99.9	> 99	> 99.9	> 99.9	> 99.9	n.c.	99.8		
Total (particulate + gaseous)	n.c.	n.c.	95	n.c.	97	> 99.9	n.c.	n.c.	n.c.	85		

n.c.: Not calculated, because relevant concentrations were below the limit of determination.

79%. The concentrations of the trace elements in plant HB, even upstream of the FGD, were in most cases too low to enable such calculations. In general, the concentrations of the elements in the flue gases upstream and downstream of FGD are so low that the estimation of collection efficiencies is associated with considerable uncertainty.

6. Discussion

6.1. Enrichment of the elements

On the basis of our experimental results, the investigated elements can be divided into three groups according to the principles reviewed by Clarke and Sloss [13] and according to the enrichment classification presented by Meij [6] (see Section 1). The classification presented by Meij [6] is shown together with the classification based on the results of this work in Table 9. In general, the observed enrichment factors were fairly well in compliance with those reported by Meij [6]. The deviations observed are assumed to be partly due to the different origin of the coal: in this work, Polish coal was used as fuel, while in the work of Meij, East American coal was used.

Mn is found to fall into group I in both plants of this study, as expected. In plant HB, Be shows intermediate behaviour between groups I and II, while according to the results of Meij [6] it falls to group II. Clarke and Sloss [13] present a similar intermediate behaviour for Be as that observed in plant HB in this study.

Considering group II, the results of this study are congruent with those of Meij [6] for all the elements studied except for Cr and Ni, which fall between groups I and II. This intermediate classification of Cr and Ni is supported by other studies [13]. However, the possible analytical and/or contamination problems discussed above can influence the results for Cr and Ni. Generally, a strong enrichment of the elements belonging to group II is not observed downstream of semi-dry FGD any more, which partly agrees with the results reported by Meij for wet FGD [6].

Considering group III (most strongly volatilising elements), a high enrichment of Hg (and Se in plant SB) in the fly ash particles is observed. The enrichment of Hg in fly ash particles was not reported by Meij. In general, Polish coal, which was used in the present study, contains more calcium than, e.g., American coal. This may lead to

Table 9

Classification of selected trace elements into different groups as presented by Meij [6], and as obtained in this study. Classification is based on the calculated enrichment factors in bottom ash, ESP ash and particulate fraction of flue gases upstream of the FGD

	Meij [6]	This work	
		Plant SB	Plant HB
Group I	Mn	Mn	Mn
Group II	As, Be, Cd, Co, Cr, Ni, Pb, Tl, V, Zn	As, Be, Cd, Co, Cr ^b , Cu, Hg, Ni ^b , Pb, Se	As, Be ^a , Cd, Cr ^{a, b} , Hg, Ni ^b , Pb, Tl ^c , Zn
Group III	Br, Hg, Se		

^aBetween groups I and II.

^bRE in the bottom ash is inconsistent with the results presented by Meij [6].

^cConcentrations in flue gases under detection limit.

increased adsorption of Hg. In plant HB, where coal with an exceptionally high ash content was used, not only the enrichment of Hg in fly ash but also its enrichment in bottom ash is stronger than expected on the basis of the results presented by Meij [6].

6.2. Mass balances

The objective of the Electric Power Research Institute (EPRI, USA) for the material balance closures in their research program PISCES (Power Plant Integrated Systems: Chemical Emission Studies) is that the total output stream for each element deviates less than $\pm 30\%$ from the total inlet stream.

For the whole process the closure of element balances were within $\pm 30\%$ for all the elements studied, except for chromium in plant HB. Furthermore, for Cd, Co, Cr, Cu, Hg, Mn, Ni and Pb in plant SB, and As, Be, Cd, Mn, Pb, Tl and Zn in plant HB the closure was even within $\pm 20\%$. Also, the estimated maximum uncertainties for the closures of most of the element streams were less than 30%. Using the EPRI criterion, these results can be considered highly satisfactory, i.e., the accuracy and representativeness of the sampling, sample treatment and analysis of the elements were successful. The closures for Se and Tl in plant SB could not be calculated, however, because the contents of these elements were below the limit of determination.

For the flue gas desulphurisation unit, the mass balance closures were in general poorer and the estimated uncertainties higher than over the whole plant. This can be ascribed to the scatter in the analytical results caused by the low element contents in the mass streams, or to the uncertainty in measuring exactly the mass streams in the FGD unit in plant SB. Based on the criterion of EPRI ($\pm 30\%$), satisfactory closures over the FGD were obtained for As, Hg, and Pb in both plants, for Cd, Co, Cr, Cu and Mn in SB, and for Zn in HB. The closures for Be, Se and Tl in plant SB and for Tl in plant HB could not be calculated.

6.3. Trace element emissions into the environment

Most of the harmful trace elements leaving the combustion process are associated with the particulate fly ash collected by the electrostatic precipitators. This ash is collected separately for potential utilisation, e.g., in the construction industry. The discharge of trace elements into the atmosphere has been strongly reduced during the last decade—thanks to the effective control of particulate flue gas emissions. In the present situation, the gaseous fraction plays a dominant role in the atmospheric trace element emissions. When aiming at further improvement of control efficiency, attention should be focused on volatile elements.

High amounts of Hg—which is an element normally considered to leave coal-fired power plants in the gas phase—were found in solid mass streams leaving the plant. Differences between plants SB and HB were observed in the behaviour of Hg: A higher amount of Hg was emitted to the atmosphere from plant SB than from plant HB. On the contrary, more Hg left plant HB in solid mass streams (almost 100% of the total input) compared to plant SB (71% of the total input). This may be explained by the much higher ash content of the coal used in plant HB, as discussed already in Section 6.1.

Another striking feature was the relatively high amount of Be—an often-neglected

element—entering the plant in the coal stream and coming out of the plant mainly in ESP ash. It is important to include Be in the emission studies because of its toxicity.

When comparing the atmospheric emission levels obtained in this study for plants equipped with semi-dry FGD to those for a plant equipped with wet FGD [6], it can be concluded that the contents of most elements in the particulate phase are approximately in the same level, i.e., very low. Meij [6] reports the vapour phase concentrations only for As, Hg and Se, which (with an exception of As) are somewhat higher than concentrations measured in this study. In this study, detectable gaseous phase concentrations downstream of the FGD were measured for Cd, Cr, Cu, Hg, Mn, Ni, Pb in the plant SB and Cd, Hg, Mn and Zn in plant HB.

7. Conclusions

Atmospheric emissions of trace elements from the plants studied, which are equipped with low- NO_x -burners, electrostatic precipitators and spray-dryer-type (semi-dry) flue gas desulphurisation, (FGD) are very low; most of them orders of magnitude less than $10 \mu\text{g}/\text{m}^3$ (NTP, i.e., normal temperature and pressure: 0°C and 1 atm). The emissions are low also for the most volatile elements, like Hg and Se. The vaporous fraction generally plays a predominant role in the trace element emissions into the atmosphere. Further reduction of trace element emissions into the atmosphere can only be accomplished if techniques capable of removing vaporous elements more effectively are developed.

High ash content of the coal seems to reduce the atmospheric emission levels of trace elements.

Be—an often-neglected, but toxic element—can enter the plant along with coal and leave it in the ash of electrostatic precipitator in relatively high amounts and should therefore be included in the environmental studies.

Mass balance closures imply that sampling and analytical techniques developed for this work can be well applied to quantitative mass balance studies in coal-fired power plants. Development is still required for the measurement of very low contents of elements.

The developed methodology to reliably determine the partitioning of the trace elements into different mass streams justifies a further quantitative analysis of the chemical form, solubility etc. This, in turn, facilitates the assessment of the environmental impacts and the overall optimisation of the operation of the whole plant.

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