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# DISTRIBUTION OF SELECTED TRACE ELEMENTS IN DUST CONTAINMENT AND FLUE GAS DESULPHURISATION PRODUCTS FROM COAL-FIRED POWER PLANTS

JAN KONIECZYŃSKI[1], ELWIRA ZAJUSZ-ZUBEK[2]

[1] Institute of Environmental Engineering of the Polish Academy of Sciences,
M. Skłodowskiej-Curie str. 34
41-819 Zabrze, Poland

[2] The Department of Air Protection,
Silesian Technical University in Gliwice,
Akademicka str. 2
44-100, Gliwice, Poland
*Corresponding author‘s e-mail: elwira.zajusz-zubek@polsl.pl

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**Abstract:** Trace elements contained in coal escape with flue gas from energy sources into the air or move towards other components of the environment with by-products captured in electrofilters (EF) and flue gas desulphurisation (FGD) plants. The existing knowledge about the distribution of frequently dangerous trace elements contained in these products is insufficient. Studies were therefore undertaken in selected power plants to investigate the distribution of trace elements in coal, slag, as well as dust containment and flue gas desulphurisation products, such as fly ash captured in dust collectors, desulphurisation gypsum and semi-dry scrubbing FGD products. Using the technique of flame atomic absorption spectrometry (F-AAS) and mercury analyser, the following were determined in the research material samples: Cr, Cu, Hg, Mn, Ni, Pb and Zn. The studies have a reconnaissance character. The authors have presented the results of determinations for selected trace elements in samples taken at Jaworzno III and Siersza Power Plants, which burn hard coal, and in Bełchatów Power Plant, burning brown coal. A balance of the examined trace elements in a stream of coal fed into the boiler and in streams of waste and products carried away from the plant was prepared. The balance based on the results of analyses from Bełchatów Power Plant was considered encouraging enough to undertake further investigations. The research confirmed that due to the distribution in the process of coal combustion and flue gas treatment, a dominant part of particular trace elements' stream moves with solid waste and products, while air emission is marginal. Attention was paid to the importance of research preparation, the manner of sample taking and selection of analytical methods.

## INTRODUCTION

Several trace elements, including mercury, have been deemed dangerous for people (Hazardous Air Pollutants) [16] and for this reason their emission should be eliminated or significantly limited. A considerable part of dangerous elements' emissions comes from production processes and coal-based power generation. For example, in Poland more than half of mercury emissions are estimated to come from these sources.

Trace amounts of minor elements contained in coal escape with furnace flue gas or waste gas from processing operations, or move towards other components of the environment through processing products or combustion by-products, such as ash, slag and FGD gypsum. The latter, when stored or used for economic purposes, may cause secondary contamination of the environment. Given the fact that Polish power industry is based on hard and brown coal and air pollution has a transboundary character, the significance of the undertaken investigations goes beyond the domestic issues. The behaviour of trace elements in the process of coal combustion for power generation needs has been subjected to numerous studies. Researchers have defined general tendencies in the distribution of trace elements in the coal combustion process in three streams: solid waste, fly ash and in the form of vapours escaping with waste gas. This is influenced by the properties of trace contaminations and the efficiency of dust containment systems [9]. The efficiency of capture of many trace elements in the solid phase approaches total dust containment efficiency. In the combustion process some elements contained in coal, such as manganese, beryllium and chromium, are only slightly enriched in ash; a greater degree of enrichment was observed in the case of antimony, lead, nickel and selenium, whereas the highest degree of enrichment was noted for arsenic and cadmium [14]. The efficiency of electrofilter dust containment drops as the size of dust grains decreases. The fly ash captured in a bag filter contained more trace elements than that arrested in an electrofilter [6]. Although the amount of trace elements emissions is chiefly influenced by dust removal efficiency, in the case of arsenic a strong effect of flue gas temperature is observed [7]. A relative drop in the efficiency of small dust fractions containment is not so noticeable in the case of bag filters. However, even if PTFE membranes are used, the efficiency of filtration drops as the size of grains diminishes [1].

The wide use of flue gas desulphurisation plants has also contributed to a decrease in dust emissions. An FGD plant, usually based on the wet limestone method, located behind the electrofilter, plays also the role of second-stage dust removal with total filtration efficiency reaching 80%. Behind the FGD plant the submicron mass fraction increases to 50%; this, however, concerns the residual emission of fly ash, accounting for no more than 0.05% of the total amount of ash produced in the coal combustion process. Nevertheless, trace elements deposited on fine dust particles penetrate through an FGD system and escape to the air [11]. The emission rates for low volatility elements depend directly on the efficiency of dust containment and flue gas treatment [17]. An important factor in the evaluation of a hard or brown coal-fired power plant is PM 2.5 dust emission due to the presence of dangerous substances in dust particles: PAHs, dioxins and heavy metals, as well as the ability of dust to penetrate into an organism via respiratory tracks. The presence of respirable dust in the air poses a health hazard [3]. According to US estimates, this causes the death of 15 000 premature babies annually [8]. The application of an efficient electrofilter and wet FGD in power and heating boilers has considerably reduced the threat caused by trace elements emissions [10, 13]. Since trace elements accumulate in dust containment and flue gas desulphurisation products, recently an increasing attention has been paid to the effects of the washing out of toxic components, including trace elements from transported [12], deposited and utilized ashes, both fresh and old, which are obtained at different coal combustion temperatures [4]. These investigations are of practical importance, but also allow discovering the way in which trace elements are bonded with organic and mineral coal substance [5, 17]. Investigations included Fate of Hg in FGD by-products. Results indicated no Hg desorbed during gypsum drying and nearly complete Hg retention during the wallboard manufacturing process and ultimate disposal. As for fly ash, the results indicate that little to no Hg would be released under normal disposal conditions [2]. So far investigations focused only on the distribution of trace elements in coal combustion and flue gas treatment by-products have not been undertaken, except for Tolvanen's study [15].

## EXPERIMENTAL PART

### *The research concept*

Power industry waste in countries using a lot of coal makes the environment considerably contaminated with trace element compounds, including heavy metals. Following the advances in flue gas containment technologies, the emission of dust from power plants fired with hard or brown coal has decreased. Slag and fly ash captured in boilers and dust containment equipment is utilized or stored on waste dumps, and only 0.2% to 0.5% of fly ash penetrates into the air. The wide use of FGD plants, in particular by the wet limestone method, has contributed to a further reduction in dust emissions. The existing knowledge of particular trace elements' distribution in coal combustion products in power plants is not sufficient. It is therefore increasingly important to obtain more information on the distribution of trace elements in real industrial conditions: in coal, slag, as well as in flue gas containment and desulphurisation by-products: fly ash arrested in dust containment equipment, desulphurisation gypsum and desulphurisation sludge treatment residue as well as in the semi-dry scrubbing FGD product. Samples of the material to be tested were taken in compliance with the standards in force; averaged analytical samples were separated. Using instrumental methods, such as F-AAS and mercury analyser, the following were determined: Cr, Cu, Hg, Mn, Ni, Pb and Zn. Technical and elementary coal analyses were also conducted.

### *Selection of plants and research material*

Three power plants having a big share in the production of electrical energy in Poland were selected for investigations. These are high standard facilities in terms of equipment and maintenance. Two of them burn hard coal, and one – brown coal. The power plants meet the requirements of environmental protection standards. The boilers with pulverized-fuel fired furnaces subjected to investigations are equipped with effective electrofilters and FGD systems (Tab. 1), so they meet the requirements related to the undertaken studies. They allow for collecting research material in a form of coal, slag, fly ash captured in electrofilters, lime and limestone used for flue gas desulphurisation and FGD by-products: gypsum and sludge residue from a wet FGD system as well as a semi-dry scrubbing FGD product.

The selected power stations have been described below.

**Siersza Power Plant**, having a total power of 820 MW, is a condensing power plant with a closed circulation system, fired with coal sludge and hard coal which has a calorific value of 21 MJ/kg and is obtained from several mines. The power plant has six blocks, four of which are equipped with 120-MW pulverized-fuel boilers working in subcritical conditions. The investigations were carried out in the boiler equipped with a modernized 99.6% efficiency electrofilter removing dust from flue gas before the process of desulphurisation by the semi-dry scrubbing method, using whitewash according to the technology developed by General Electric Environmental Systems Inc., and with a bag filter which captures dust from the desulphurised flue gas. The FGD by-product is extracted from the reactor and combined with the product dust captured in a bag filter. The efficiency of desulphurisation reaches no less than 87%, and the concentration of dust in flue gas carried away into the chimney does not exceed the standard value of 50 mg/m$^3$.

**Jaworzno III Power Plant,** having a total power of 1345 MW, is equipped with six 220–225 MW blocks with pulverized-fuel boilers working in subcritical conditions. It is a condensing power plant with a closed circulation system, fired with hard coal having a calorific value of 23.1 MJ/kg, which is obtained from several mines. The boiler plants are equipped with 99.5% efficiency electrofilters and wet FGD systems (Steinmüller technology) reaching 95% desulphurisation efficiency. Gypsum produced in the FGD process is sold to the processing industry.

**Bełchatów Power Plant**, generating 18.5% of electrical energy in Poland, having a total power of 4440 MW, is a condensing power plant with a closed circulation system, fired with brown coal from the neighbouring opencast mine, which has a calorific value of 8 MJ/kg. The power plant is equipped with 12 power blocks, each having a power of 360 MW, with pulverized-fuel boilers working in subcritical conditions. In all the blocks flue gas dust is captured by 99.6% efficiency electrofilters and sulphur is removed by the wet limestone method according to the General Electric Environmental Systems Inc. technology, reaching the efficiency of 94%. The gypsum produced in the process is sold to Knauf processing plant. Coarse-grained ash and slag from the boilers is transported to furnace waste grounds, whereas ash from ash hoppers under the electrofilters is transported to the mine, where after mixing with the overlay, it is deposited in the excavation.

Table 2 presents basic data on the mass stream of coal, absorbents and dust containment products: slag and ash captured in an electrofilter as well as semi-dry scrubbing FGD product or gypsum – the data refers to 3 examined blocks.

Table 1. Characteristics of the boilers and coal

| Power plant | Type of boiler | Coal | Ash content, % w/v | Flue gas dedusting | Flue gas desulphurisation |
|---|---|---|---|---|---|
| Siersza | OP 380 | hard coal | 19.8 | EF | dry scrubbing |
| Jaworzno III | OP 650 | hard coal | 21.2 | EF | limestone / gypsum |
| Bełchatów | BB 1150 | brown coal | 8.8 | EF | limestone /gypsum |

Table 2. The consumption of coal and absorbents, combustion and FGD solid products in the examined boilers, t/h

| Power plant | Coal | Limestone/ Lime | Slag | Fly ash | Dust emitted with flue gases | FGD products |
|---|---|---|---|---|---|---|
| Siersza | 45 | 1.19 | 2.37 | 6.51 | 0.011 | 1.93 |
| Jaworzno III | 87 | 5.61 | 4.17 | 12.50 | 0.028 | 9.48 |
| Bełchatów | 380 | 20.60 | 1.9 | 30.78 | 0.120 | 34.63 |

***The method of sample taking and sample preparation for analyses***

In order to prepare samples for further analysis, the research material was properly taken, separated or processed by using appropriate methods and procedures. In power plants fired with hard coal, samples were taken during one production shift (8-hour) for two days. After the coal samples had been ground in a coal mill, they were taken manually from the boiler feed system. Slag samples were taken manually from the boiler deslagging system. Fly ash samples were taken manually from the system extracting the ash from the electrofilter. Lime for semi-dry scrubbing FGD was taken manually from the absorption slurry preparation system. Similarly, limestone for wet limestone FGD was taken from the absorption slurry preparation system. The product of flue gas desulphurisation by the semi-dry scrubbing method was taken manually from the system of flue gas extraction from the bag filter, and gypsum was taken manually from the FGD vacuum filter. Residue from FGD sludge treatment plant was taken manually from the sludge residue separation vacuum filter. In the case of power plant fired with brown coal, a mechanical probe for continuous sampling of coal from the belt conveyor flight transporting fuel from the opencast mine was used. The collected samples were ground and separated for analysis. For the needs of these investigations, 24-h averaged samples of brown coal from the boiler carburizing process (K5 to K8 boilers of the same type) were taken.

Slag samples from the boiler deslugging system (K5 to K8 boilers) were taken, ground and averaged. Samples of fly ash from the system extracting the ash precipitated in electrofilters dedusting flue gas from K5 to K8 boilers were taken, ground and averaged. Samples of limestone slurry from the FGD feed mill installed on K5 to K8 boilers were taken and averaged. Samples of gypsum which was produced in the FGD plant installed on K5 to K8 boilers and separated on the vacuum filter were taken, ground and averaged. For the needs of this study, 24-h averaged samples of slag, fly ash, limestone slurry and gypsum were prepared. The samples were taken during 5 days for two weeks. The following samples were prepared for analysis by averaging and grinding the same kind of samples from five daily sets:

– samples of hard and brown coal burned in the examined plants;
– samples of slag from pulverized coal fired furnaces used in the examined plants;
– samples of fly ash from pulverized coal fired furnaces captured in the electrofilter and transported to the waste dump or utilized;
– samples of FGD solid product from the bag filter drier in the semi-dry scrubbing FGD plant;
– samples of lime/limestone used for flue gas desulphurisation;
– samples of gypsum being the product of flue gas desulphurisation by the wet limestone method;
– residue from wet limestone FGD sludge treatment.

***Analytical methods***

**Determination of mercury in coal, slag, fly ash and flue gas desulphurisation products**

Mercury in the examined samples was determined by means of MA-2 mercury analyser produced by Nippon Instruments Corporation. The method involves thermal decomposition of a sample; mercury content is measured by atomic absorption spectrometry – using the cold vapour method (CV-AAS). This method is characterized by high accuracy, the error of determination reaching 0.002 ng.

The correctness of mercury content determination was verified using Standard Reference Material 1632c; Trace Elements in Coal (bituminous); U.S. Department of Commerce; National Institute of Standards and Technology, Gaithersburg, MD 20899.

**Determination of Cr, Cu, Mn, Ni, Pb and Zn in coal, slag, fly ash and flue gas desulphurisation products**

Solid samples having a mass of 0.15 g were dissolved in a Multiwave 3000 microwave mineralization unit produced by Anton Paar, in a mixture of acids which allowed for obtaining a clear solution. In the case of hard and brown coal, slag, fly ash and semi-dry scrubbing FGD solid product, the samples were mineralized in two stages. In the first stage a mixture of nitric, perchloric acid and hydrofluoric acids was used. In the second stage, boric acid was added to the reaction vessel. In the case of limestone, lime, gypsum and wet limestone FGD sludge treatment residue, one-stage mineralization in a mixture of nitric, perchloric and hydrochloric acids was applied. After dissolving, the whole amount of the solution was poured into a 50 $cm^3$ measuring flask and filled up with deionised water to nominal volume. In so obtained solutions the concentrations of selected trace elements were determined using the method of flame atomic absorption spectrometry, by means of an AVANTA PM spectrometer produced by GBC Scientific Equipment. The reagents *for trace analysis* produced by Fluka were used to prepare the samples and reference samples.

## RESEARCH RESULTS AND DISCUSSION

Table 3 presents the results of determinations of trace elements concentration in the analytical samples of coal burned in the examined plants. Given the known difference in the content of trace elements in coal depending on the type, the place of origin, coal bed and other factors, it may be stated that the concentrations of Cr, Cu, Mn, Ni and Pb in hard and brown coal are similar. The biggest difference is observed in the case of zinc: from 8 ppm in brown coal to 144 ppm in coal burned in Siersza Power Plant. Mercury has a lower concentration level, below 1 ppm. The highest concentration of mercury was found in brown coal: 516 ppb, lower in hard coal: 153 and 184 ppb.

Concentrations of the investigated trace elements in coal and ash were compared and enrichment coefficients were calculated. Table 4 presents the values of enrichment coefficient $EC_{i_{a/c}}$ as a $c_{ia}/c_{ic}$ ratio.

The enrichment coefficient reached its lowest value in the case of mercury, which may be attributed to mercury volatility.

Concentrations of the examined trace elements in ash and slag were also compared by calculating $EC_{i_{s/a}}$ – the enrichment coefficient of element *i* in slag in relation to ash, $c_{is}/c_{ia}$ (Tab. 5).

The results given in Table 5 confirm the influence of temperature in particular furnace zones. The relative impoverishment of slags compared to ashes is linked to the higher temperature of the furnace lower part, where slag is deposited. The above mentioned slag impoverishment is particularly visible in the case of mercury.

Mercury released in the process of coal combustion is captured in wet limestone FGD, which has been confirmed by the results of analysis conducted for gypsum produced in an FGD plant.

Table 3. Concentrations of selected trace elements in coal, slag, ash and flue gas desulphurisation products

| Plant | Type of substance | Cr, ppm | Cu, ppm | Hg, ppb | Mn, ppm | Ni, ppm | Pb, ppm | Zn, ppm |
|---|---|---|---|---|---|---|---|---|
| Siersza | hard coal | 16.6 | 15.7 | 153 | 34.0 | 15.7 | 44.9 | 143.6 |
| | slag | 103.5 | 88.6 | 184 | 249.3 | 68.5 | 56.2 | 242.6 |
| | ash | 128.7 | 100.4 | 478 | 272.3 | 116.9 | 179.9 | 485.4 |
| | lime | 1.1 | 5.7 | 62 | 74.5 | 0.2 | 314.6 | 32.4 |
| | FGD product | 5.0 | 15.6 | 81 | 94.9 | 0.1 | 22.2 | 112.8 |
| Jaworzno III | hard coal | 9.9 | 14.0 | 184 | 12.2 | 9.4 | 7.6 | 54.5 |
| | slag | 92.2 | 101.8 | 37 | 554.6 | 49.9 | 46.9 | 147.4 |
| | ash | 110.8 | 133.4 | 272 | 549.7 | 59.3 | 147.3 | 339.3 |
| | limestone | 3.2 | 4.6 | 57 | 60.5 | 4.8 | 27.7 | 68.1 |
| | gypsum | 2.2 | 6.3 | 327 | 2.1 | 0.1 | 66.8 | 8.5 |
| | FGD sludge residue | 47.3 | 126.9 | 7 538 | 2 281.4 | 61.3 | 301.1 | 1 388.6 |
| Bełchatów | brown coal | 13.2 | 9.7 | 516 | 38.8 | 6.4 | 13.7 | 8.3 |
| | slag | 91.5 | 46.6 | 32 | 115.1 | 30.1 | 20.9 | 65.9 |
| | ash | 105.8 | 56.1 | 125 | 179.2 | 41.4 | 22.5 | 70.1 |
| | limestone | 0.1 | 4.7 | 7 | 0.1 | 8.7 | 9.7 | 0.2 |
| | gypsum | 3.1 | 3.0 | 2 411 | 5.5 | 3.5 | 4.1 | 2.2 |

Table 4. Enrichment coefficients of element *i* in ash in relation to coal

| Power plant | $EC_{Cr\ a/c}$ | $EC_{Cu\ a/c}$ | $EC_{Hg\ a/c}$ | $EC_{Mn\ a/c}$ | $EC_{Ni\ a/c}$ | $EC_{Pb\ a/c}$ | $EC_{Zn\ a/c}$ |
|---|---|---|---|---|---|---|---|
| Siersza | 7.8 | 6.4 | 3.1 | 8.0 | 7.4 | 4.0 | 3.4 |
| Jaworzno III | 11.2 | 9.5 | 1.5 | 45.1 | 6.3 | 19.4 | 6.2 |
| Bełchatów | 8.0 | 5.8 | 0.2 | 4.6 | 6.5 | 1.6 | 8.4 |

Table 5. Enrichment coefficients of element *i* in slag in relation to ash

| Power plant | $EC_{\mathrm{Cr\ s/a}}$ | $EC_{\mathrm{Cu\ s/a}}$ | $EC_{\mathrm{Hg\ s/a}}$ | $EC_{\mathrm{Mn\ s/a}}$ | $EC_{\mathrm{Ni\ s/a}}$ | $EC_{\mathrm{Pb\ s/a}}$ | $EC_{\mathrm{Zn\ s/a}}$ |
|---|---|---|---|---|---|---|---|
| Siersza | 0.8 | 0.9 | 0.4 | 0.9 | 0.6 | 0.3 | 0.5 |
| Jaworzno | 0.8 | 0.8 | 0.1 | 1.0 | 0.8 | 0.3 | 0.4 |
| Bełchatów | 0.9 | 0.8 | 0.3 | 0.6 | 0.7 | 0.9 | 0.9 |

The enrichment coefficient of gypsum compared to ash $EC_{i_{g/a}}$ *as a* $C_{ig}/C_{ia}$ is more than 1 (Tab. 6) only in the case of mercury. A very high value of $c_{ig}/c_{ia}$ determined for Bełchatów Power Plant might be due to the exceptionally high content of moisture in flue gas.

Table 6. Enrichment coefficients of element *i* in gypsum in relation to ash

| Power plant | $EC_{\mathrm{Cr\ g/a}}$ | $EC_{\mathrm{Cu\ g/a}}$ | $EC_{\mathrm{Hg\ g/a}}$ | $EC_{\mathrm{Mn\ g/a}}$ | $EC_{\mathrm{Ni\ g/a}}$ | $EC_{\mathrm{Pb\ g/a}}$ | $EC_{\mathrm{Zn\ g/a}}$ |
|---|---|---|---|---|---|---|---|
| Jaworzno III | 0.020 | 0.047 | 1.202 | 0.004 | 0.002 | 0.453 | 0.025 |
| Bełchatów | 0.029 | 0.053 | 19.288 | 0.031 | 0.085 | 0.182 | 0.031 |

The level of trace elements' capture in a wet limestone FGD plant is higher than that indicated by the analysis of gypsum produced. Gypsum suspension obtained in an FGD absorber is dehydrated by means of a vacuum filter. During this procedure a layer of gypsum on a filter tape is washed with water. Washings are thickened in a separate FGD sludge treatment plant. Solid waste is utilized in an environmentally friendly way. The results of analysis of FGD waste in Jaworzno III Power Plant have been presented in Tab. 7. Due to unavailability of other data, these results ($EC_{i_{w/g}}$ indicators – in waste compared to gypsum) cannot be used in a trace element balance. Nevertheless, the analysis results contained in Table 7 show the importance of wet flue gas desulphurisation in the distribution of trace elements in coal-based power generation processes.

Table 7. Enrichment coefficients of element *i* in waste in relation to gypsum

| Power plant | $EC_{Cr\ w/g}$ | $EC_{Cu\ w/g}$ | $EC_{Hg\ w/g}$ | $EC_{Mn\ w/g}$ | $EC_{Ni\ w/g}$ | $EC_{Pb\ w/g}$ | $EC_{Zn\ w/g}$ |
|---|---|---|---|---|---|---|---|
| Jaworzno III | 21.5 | 20.1 | 23.1 | 1086.4 | 613.0 | 4.5 | 163.4 |

The investigations into trace elements' distribution in coal combustion, dust containment and flue gas desulphurisation by-products should be crowned with a balance of particular elements. It consists in comparing a stream of element *i* introduced into and carried away from the power plant equipped with dust removal and FGD systems, surrounded with an installed balance shield.

The mass stream *S* of element *i* (introduced or carried away) is the product of concentration *c* of element *i* in raw material, product or waste *m* and stream *s* of material *m*:

$$S_{im} = c_{im} \cdot s_m \qquad [\text{kg/h}]$$

Concentrations *c* are expressed in mg/kg, or mg/m$^3$ for solid materials, gases and liquids.

The total mass stream $S_T$ of element *i* introduced or carried away with particular streams of raw material, products or waste is defined by the following sum:

$$S_{iT} = \Sigma S_{im}$$

The total stream $S_{iTin}$ (introduced) is compared with total stream $S_{iTout}$ (carried away). The indexes *i* and *o* refer to input and output mass respectively.

The closure of each element mass balance *B* is defined by the following equation:

$$B = \frac{S_{iTn}}{S_{iTout}} \cdot 100\%$$

In order to carry out balance works, it is necessary to analyse streams introduced in the systems. They include: coal, water for wet FGD and limestone or lime needed to prepare an absorption suspension, whereas streams carried away from the system include: slag, fly ash captured in an electrofilter, gypsum or another desulphurisation product, FGD sludge and desulphurised flue gas. When conducting investigations, the authors did not have access to the means ensuring the fulfilment of all the requirements. Water and desulphurised gases were not analysed, so the balance does not contain data on the amount of dust emitted into the air and on the concentration of trace elements contained in dust and in the gaseous form of flue gas emissions.

The data contained in Table 2 indicate that solid products, including ash, slag and gypsum or wet FGD by-products account for more than 99% of waste produced in the process of coal-based power generation, whereas dust which penetrates through dust containment and flue gas desulphurisation systems and escapes with flue gas is a mere fraction of a percent (Tab. 8).

Table 8. Waste and solids from the coal-fired power plant

| No. | Power plant | % w/w fraction | |
|---|---|---|---|
| | | Solid products* | Dust emitted with flue gases |
| 1 | Siersza | 99.9 | 0.10 |
| 2 | Jaworzno III | 99.83 | 0.17 |
| 3 | Bełchatów | 99.63 | 0.37 |

* ash, slag, gypsum, dry scrubbing FGD product

It has to be emphasised that the lack of data on the stream of the examined trace elements in desulphurised flue gas has little influence on the final balance. This results from a very low content of dust in desulphurised flue gas. As revealed in current research, the concentration of dust in flue gas desulphurised by the wet method does not exceed 10 mg/m$^3$, and in new modern plants even 5 mg/m$^3$. Therefore, the $PM_{10}$ emission of dust from a power block fired with hard coal reaches a maximum of 0.02% [10]. The concerns that flue gas contains significant amounts of the examined elements' vapours are not justified either. The analysis of an FGD waste stream was conducted solely for Jaworzno III Power Plant. However, there was no possibility to quantitatively determine the size of trace elements' streams contained in this waste. Due to the low research budget, the material taken in Jaworzno III and Siersza Power Plants does not fulfil all representativeness rigours in terms of the sampling time and the number of identical samples. The data on the amount of slag and ash carried away from the electrofilters which was obtained from these power plants is only approximate. Due to financial limitations, only 3 instead of 5–7 repeat analyses were conducted.

For the same reasons, a balance was presented only for Bełchatów Power Plant (Tab. 9), which fulfils all the above mentioned requirements. The balance was based on the stream of coal, slag, ash captured in electrofilters and gypsum as well as the concen-

Table 9. The balance of trace elements in K5–K8 boiler plants at Bełchatów Power Plant

| Type of mass stream | Input / output | Trace elements, g/h | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Cu | Hg | Mn | Ni | Pb | Zn |
| Coal | $S_{iTin}$ | 2257.20 | 1658.70 | 88.24 | 6634.80 | 1094.40 | 2342.70 | 1419.30 |
| Limestone | | 2.06 | 96.82 | 0.14 | 2.06 | 179.20 | 199.82 | 4.12 |
| Water | | *no data available* | | | | | | |
| Total | | 2259.26 | 1755.52 | 88.38 | 6636.86 | 1273.60 | 2542.52 | 1423.42 |
| Slag | $S_{iTout}$ | 173.85 | 88.54 | 0.06 | 218.69 | 57.19 | 39.71 | 125.21 |
| Ash | | 3256.52 | 1726.76 | 3.85 | 5515.78 | 1274.29 | 692.55 | 2157.678 |
| Gypsum | | 107.35 | 103.89 | 83.49 | 190.47 | 121.21 | 141.983 | 76.186 |
| Flue gas | | *no data available* | | | | | | |
| Total | | 3537.73 | 1919.19 | 87.40 | 5924.93 | 1452.69 | 874.24 | 2359.07 |
| The closure of the mass balance, % | | 148.6 | 109.3 | 98.9 | 89.3 | 114.0 | 34.4 | 165.7 |

trations of the examined trace elements in these substances. Due to exceptionally high – reaching 55% content of moisture in brown coal (data of Bełchatów Power Plant), the coal mass stream was converted into dry matter.

On the basis of data on mass streams of selected trace elements, their mass fractions in slag, fly ash and FGD gypsum were calculated. The results of calculations have been presented in Table 10. Taking into consideration the fact that the balance does not include the stream of the examined substances introduced with water and the streams carried away with the emitted dust and gaseous substances, the obtained results were quite consistent. The content of slag in the distribution of elements excluding mercury and lead ranges from 3.7 to 5.3% w/w, fly ash – 87.7 to 93.1% w/w, and gypsum – 3.0–8.3% w/w. The high level of mercury release in the process of coal combustion is confirmed by its scant content in slag, a little fraction in fly ash and a very high content in gypsum. The content of lead in gypsum is notably higher compared to Cr, Cu, Mn, Ni and Zn.

Table 10. Distribution of selected trace elements in slag, fly ash and FGD gypsum at Bełchatów Power Plant (K5–K8 boilers), in %

| Type of substance | Distribution of trace elements, in % | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cr | Cu | Hg | Mn | Ni | Pb | Zn |
| Slag | 4.9 | 4.6 | 0.1 | 3.7 | 3.9 | 4.5 | 5.3 |
| Ash | 92.0 | 90.0 | 4.4 | 93.1 | 87.7 | 79.2 | 91.5 |
| Gypsum | 3.0 | 5.4 | 95.5 | 3.2 | 8.3 | 16.2 | 3.2 |

***Summary***

The conducted studies have a reconnaissance character. The level of balance ranging from 70 to 130% should be considered a satisfactory result. Such a result was obtained for mercury, manganese, copper and nickel. The balance of mercury is very good. The balance of chromium is worse, and that of lead and zinc – unsatisfactory. Despite these imperfections, the results of work have confirmed that investigations into trace elements distribution provide additional information which allow for evaluating the arduousness to environment caused by hard and brown coal combustion in power plants, especially if this arduousness is to be assessed in terms of *life cycle*. The results obtained in three representative power plants have revealed that potential environmental threats due to trace elements contained in coal fuel are chiefly related to solid waste and products. The investigations have showed that the obtaining of satisfactory results requires careful planning, preparation and the taking of samples of coal, combustion, dust containment and FGD products as well as the analysis of rigorously averaged samples from several measurement sessions. Trace elements should be determined using the AAS or ICP method. Analyses should be repeated minimum five times. It is recommended that the results of analyses be verified by another laboratory. Probably the very good balance of mercury was partly due to the use of a special mercury analyser. A balance requires precise data on fuel consumption and the stream of products and waste. Such data is not available in all plants subjected to investigations. The final balance must be based on determinations of substances in the emitted dust and substances escaping with flue gas in a gaseous form, which requires a suitable probe.

## CONCLUSIONS

- Investigations conducted in selected coal-fired power plants have confirmed that if efficient dust containment equipment and FGD plants are applied, more than 99% w/v of the investigated trace elements move from the fuel towards solid waste and combustion products.
- The distribution of a particular trace element in waste as well as in combustion, dust containment and FGD products is specific of this element.
- Mercury, a high volatility element, was accumulated in gypsum, which confirms a significant role that an FGD plant plays in the process of dust containment and flue gas treatment apart from its flue gas desulphurisation function.
- When the high requirements for sampling under operating conditions in power plants are fulfilled, it is possible to prepare a satisfactory balance of particular trace elements.
- Investigations into trace elements distribution enable to evaluate the arduousness of a coal-fired power plant in terms of *life cycle*.

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## DYSTRYBUCJA WYBRANYCH PIERWIASTKÓW ŚLADOWYCH W PRODUKTACH ODPYLANIA I ODSIARCZANIA SPALIN Z ELEKTROWNI OPALANYCH WĘGLEM

Występujące w węglu pierwiastki śladowe uchodzą ze spalinami ze źródeł energetycznych do powietrza lub przemieszczają się do innych elementów środowiska poprzez produkty uboczne zatrzymane w urządzeniach odpylających i instalacjach odsiarczania spalin. Dotychczasowa wiedza o dystrybucji pierwiastków śladowych, często niebezpiecznych dla ludzi, w tych produktach jest niewystarczająca. W związku z tym podjęto badania w wybranych elektrowniach nad dystrybucją pierwiastków śladowych w: węglu, żużlu, a także w produktach odpylania i odsiarczania spalin: w popiele lotnym zatrzymanym w urządzeniach odpylających, w gipsie z odsiarczania oraz produktach z instalacji odsiarczania metodą półsuchą. W próbkach materiału badawczego, stosując metodę atomowej spektrometrii absorpcyjnej z atomizacją płomieniową F-AAS i analizator do rtęci oznaczono: Cr, Cu, Hg, Mn, Ni, Pb i Zn. Badania mają charakter rozpoznawczy. Przedstawiono wyniki oznaczeń wybranych pierwiastków śladowych w próbkach pobranych w E. Jaworzno III i E. Siersza, spalających węgiel kamienny oraz w E. Bełchatów, spalającej węgiel brunatny. Przeprowadzono próbę zbilansowania badanych pierwiastków śladowych w strumieniu węgla wprowadzanego do kotła i w strumieniach odpadów i produktów, wyprowadzanych z instalacji. Bilans przeprowadzono opierając się na wynikach analiz z E. Bełchatów i uznano za zachęcający do dalszych badań. Badania potwierdziły, że w wyniku dystrybucji w procesie spalania węgla i oczyszczania spalin dominująca część strumienia poszczególnych pierwiastków śladowych przemieszcza się z odpadami i produktami stałymi, a emisja do powietrza jest marginesowa. Zwrócono uwagę na znaczenie przygotowania badań, sposób poboru próbek i dobór metod analitycznych.