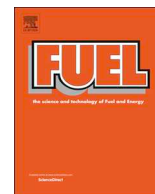




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## Full Length Article

# High mercury emission (both forms: $\text{Hg}^0$ and $\text{Hg}^{2+}$ ) from the wet scrubber in a full-scale lignite-fired power plant

 Renata Krzyżyńska<sup>a,\*</sup>, Zbyszek Szeliga<sup>b</sup>, Lukas Pilar<sup>c</sup>, Karel Borovec<sup>b</sup>, Paweł Regucki<sup>d</sup>
<sup>a</sup> Faculty of Environmental Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

<sup>b</sup> VŠB Technical University of Ostrava-CENET, 17. listopadu 15, 708 00 Ostrava-Poruba, Czech Republic

<sup>c</sup> Faculty of Mechanical Engineering, Czech Technical University in Prague, Technická 4, CZ-166 Praha 6, Czech Republic

<sup>d</sup> Faculty of Mechanical and Power Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

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## ABSTRACT

The paper describes and discusses the results of research on mercury behaviour, especially its high emission, in both forms: elemental ( $\text{Hg}^0$ ) and oxidised ( $\text{Hg}^{2+}$ ), from the wet flue gas desulphurisation scrubber (WFGD) in a lignite-fired power plant located in central Europe. The presented results involve the collection of lignite power plant samples (liquid, solid, gas) and different laboratory chemical analyses to try to understand the mechanism of mercury re-emission from the wet flue gas desulfurization system. It was noted that 67–80% of the total inlet mercury concentration left the WFGD scrubber. Moreover, the oxidised form of mercury was the main emitted form (about 60–70% of the total mercury concentration). The results show that mercury was found in very high concentration (10  $\mu\text{g}/\text{g}$ ) (range: ppm) in the WFGD solid by-products, whereas the liquid phase contained only 1  $\mu\text{g}/\text{l}$  (range: ppb). Considering literature reports and presented data from the investigated power station, we believe that iron (Fe), which occurs in very high concentrations in solid WFGD samples (1.81% wt. Fe) and lignite (up to 20 g/kg Fe) is mainly responsible for disrupting the mercury absorption in the scrubber, the partitioning of the mercury between phases and leads to its reemission. Moreover, we believe also that a relatively high iodine ion concentration (130 mg/l) in the limestone slurry leads to mercury emission in its oxidised form, mainly as  $\text{HgI}_2$ , which is highly volatile. Other minor components from limestone dissolution such as Mn, Al and Mg may additionally enhance that “complex” mercury behaviour.

## 1. Introduction

The knowledge about the wet flue gas desulphurisation scrubbers' chemistry is necessary to implement mercury control in these units. Mercury concentration in coals generally ranges from 0.05 to 0.5  $\mu\text{g}/\text{g}$ , with 0.1  $\mu\text{g}/\text{g}$  being a typical value that corresponds to the range of 10 to 20  $\mu\text{g}/\text{Nm}^3$  in the flue gases and it is typically present in the flue gas upstream of the WFGD system as a mixture of oxidised and elemental mercury ( $\text{Hg}^{+2}$  and  $\text{Hg}^0$ , respectively). Bituminous coals tend to produce mostly oxidised mercury in the flue gas, while subbituminous coal and lignite generally produce mostly elemental mercury. Oxidised mercury can be removed at a high efficiency (ex. 90% or greater) in the WFGD absorbers, limited primarily by a phenomenon called “re-emission,” and typically leaves the WFGD system with solid or liquid by-products. Elemental mercury, which is not water-soluble, typically passes through the WFGD absorber unscrubbed [2,33].

WFGD systems are known to remove a certain percentage of

mercury in the coal flue gases. This raises several questions about the fate of mercury removed by the WFGD installation: Does the absorbed mercury stay in the WFGD liquor or does it leave the unit with the solid by-products? What happens to mercury in the WFGD liquor and solid by-products when they leave the WFGD system? [1]

The paper describes the results of analyses of a collection of lignite power plant samples (liquid, solid, gas) by different laboratory chemical methods to understand the behaviour of mercury in the wet flue gas desulphurisation system (WFGD) installed in the lignite-fired power plant located in central Europe. The obtained results are very surprising and uncommon for two reasons. Firstly, because a significant amount of the oxidised form of mercury ( $\text{Hg}^{2+}$ ) left the WFGD scrubber (about 60–70% of total outlet WFGD mercury conc.), what is very unusual in such installations. It is worth to emphasize that two methods of mercury measurement were used simultaneously to control the correctness of the measurements. 30–40% of mercury emitted from the scrubber was in the elemental form ( $\text{Hg}^0$ ), at a higher percentage than at the WFGD

\* Corresponding author.

E-mail address: [renata.krzyzynska@pwr.edu.pl](mailto:renata.krzyzynska@pwr.edu.pl) (R. Krzyżyńska).

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inlet. Secondly, results show that mercury was found at a very high concentration (10 µg/g) in the WFGD solid by-products, compared to average mercury concentration in the WFGD gypsum solids samples in the literature: 0.08 – 2.75 µg/g [1], 0.143–1.167 µg/g [21], 0.33 to 2.40 µg/g [26], 0.61 – 1.63 µg/g [27], 0.75–3.27 µg/g [28].

Moreover, mercury was found mainly in the solid phase of the absorber slurry, what was somewhat surprising because, according to the literature, the oxidised form of mercury ( $\text{Hg}^{2+}$ ) is water-soluble and goes into the liquid phase [1–3]. This has been indicated by our previous laboratory studies as well [6]. We took an effort to understand that unusual situation encountered in the lignite-fired power plant and tried to find the explanation confronting this detailed discussion with a literature review.

## 2. Experimental procedure and methodology

WFGD's tests were performed in a lignite-fired power plant located in Central Europe in the Czech Republic. The investigated installation was designed to clean the boiler flue gas to the terminal value below the legislative emission limits. The flue gas cleaning system consisted of ESP (electrostatic precipitator) – four sections, limestone WFGD, primary combustion methods for NO<sub>x</sub> control. The flue gas flow capacity of the WFGD was ~1 000 000 Nm<sup>3</sup>/h. To obtain a broader insight into the mercury behaviour in the wet flue gas desulphurisation system, a lot of samples were taken and analyses were made: liquid and solid samples from the WFGD unit, the flue gas measurement with Hg speciation upstream and downstream of a desulphurisation unit (continual measurement and Ontario Hydro method), supported by lignite and ash analysis. The slurry pH and redox potential were also measured by a potentiometric method – ProMinent 305,052 red-ox – probe RHEK – Pt – S. The mineral composition of solid samples was characterised by diffractometry – X-ray diffraction (XRD) and SEM (Scanning Electron Microscope) micrographs. Diffractometric analysis was performed using the powder method (DSH) in geometry Bragg-Brentano, using the D8 DISCOVER diffractometer, Bruker, radiation CuK $\alpha$ , filter Ni, detector LYNXEYE\_XE. Mineral components in the solid samples were marked and calculated based on licensed models and databases. SEM (Scanning Electron Microscope) micrographs of solid samples were performed on a SEM SU3500 scanning electron microscope with variable vacuum, Hitachi, cooperating with an EDS UltraDry X-ray spectrometer with an energy dispersion, Thermo Scientific NORAN System 7.

The WFGD samples from the lignite-fire power plant were taken to an on-site laboratory and filtered to separate the solid and liquid phases using acid-washed glassware and quartz filters. The WFGD absorber liquor samples and absorber solids samples were analysed in the laboratory. The analytical procedures are summarised in Tables 2 and 3.

The percentage of suspended solids in the WFGD slurry was 15%.

Mercury in the flue gas was simultaneously analysed by two methods: OH (Ontario-Hydro method) and continuous measurement by Durag – Verewa I & II analyser, model HM 1400 TRX. The Durag measurement is based on atomic fluorescence spectroscopy and thermal conversion of mercury ion compounds to atomic mercury. The analyser uses the principle of a thermal reactor with a catalyst in the dry state, followed by the atomic absorption spectrometry of cold vapour CV AAS by ultraviolet radiation absorption.

For the speciation of individual forms of mercury ( $\text{Hg}^T$ ,  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ ) in the flue gas the Ontario Hydro (OH) method was used. The OH method is a standard method of measuring and speciating mercury in the flue gas. The method is based on isokinetic sampling and dust filtration. Accuracy of the method is up to 2 µg/Nm<sup>3</sup>. The flue gas concentration was measured in the inlet and outlet of the WFGD installation.

## 3. Results and discussion

This section presents the results and provides a discussion to investigate the mercury behaviour in the WFGD system in a lignite-fired boiler in a power plant. The main aim of the project was a better understanding of what happens to mercury that is absorbed in the WFGD systems, what parameters affect mercury re-emission the most and whether the absorbed mercury goes to the solid or liquid phase. The answers should be helpful in creating or choosing the best method of preventing mercury emission and re-emission from the wet scrubbers.

### 3.1. Mercury analyses in the flue gas and WFGD liquor and solid samples

Mercury in the flue gas was simultaneously analysed by both methods: OH (Ontario-Hydro method) and Durag – Verewa analyser, model HM 1400 TRX. Analysis accuracy was as in the standard procedures for the determination of trace elements. The flue gas composition was measured by continuous analysers at the inlet of WFGD and is presented in Table 1. The WFGD absorber liquor samples and absorber solids samples were analysed in the laboratory and are presented in Tables 4–6. The lignite and ash characteristics are presented in Tables 8–10. Additionally, the images of solids of the WFGD slurry are presented in Figs. 2 and 3.

Mercury in the flue gas was simultaneously analysed by two methods. Both measurements were continuously performed at the same time, and results are presented below:

$$\begin{aligned} \text{WFGD inlet} - \text{Hg}^T &= 31.4 \mu\text{g}/\text{m}^3 (\text{Hg}^0 = 85\%, \text{Hg}^{2+} + \text{Hg}_p = 15\%) \\ \text{OH method} \\ \text{WFGD outlet} - \text{Hg}^T &= 25 \mu\text{g}/\text{m}^3 (\text{Hg}^0 = 30\%, \text{Hg}^{2+} + \text{Hg}_p = 70\%) \\ \text{OH method} \\ - \text{Hg}^T &= 21 \mu\text{g}/\text{m}^3 (\text{Hg}^0 = 40\%, \text{Hg}^{2+} + \text{Hg}_p = 60\%) \text{ DURAG} \\ \text{analyser} \end{aligned}$$

Mercury concentration in lignite was 0.22 mg/kg. Mercury found in the solid phase WFGD slurry was Hg = 10 µg/g (10 ppm) and Hg = 1 µg/l (1 ppb) in the liquor phase.

In the analysed samples, the total mercury concentration ( $\text{Hg}^T$ ) in the flue gas at the inlet of the WFGD was = 31.4 µg/m<sup>3</sup>, with speciation:  $\text{Hg}^0 = 85\%$ ,  $\text{Hg}^{2+} + \text{Hg}_p = 15\%$ . The mercury flue gas concentration in the outlet of the WFGD was about 25 µg/m<sup>3</sup>, with speciation:  $\text{Hg}^0 = 30\%$ ,  $\text{Hg}^{2+} + \text{Hg}_p = 70\%$  determined by OH method and very similar speciation determined by Durag analyser:  $\text{Hg}^0 = 40\%$ ,  $\text{Hg}^{2+} + \text{Hg}_p = 60\%$ . The WFGD absorber outlet flue gas had a much higher oxidised mercury concentration ( $\text{Hg}^{2+} = 12.6\text{--}17.5\text{--}10 \mu\text{g}/\text{m}^3$ )

**Table 1**

The flue gas composition at the inlet WFGD.

Flue gas composition	Unit	Maximum case (100% WFGD load)
$\text{Hg}^T$	µg/m <sup>3</sup>	31.4
H <sub>2</sub> O vapour	vol %, wet	17.4
H <sub>2</sub> O liquid	kg/h	0
O <sub>2</sub>	vol %, dry	5.4
CO <sub>2</sub>	vol %, dry	13.8
SO <sub>2</sub> at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	11 350
SO <sub>3</sub> <sup>*)</sup> at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	75
NO <sub>2</sub> at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	200
HCl at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	39
HF at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	76
TZL/fly ash <sup>**)</sup> at 6% O <sub>2</sub>	mg/Nm <sup>3</sup> , dry	50

\*) The content of SO<sub>3</sub> is corresponding to acid dew point temperature up to max. value 150 mg/Nm<sup>3</sup>. The acid dew point is < 130–150 °C (range min. and max. load).

\*\*) Soot and little amounts of unburned substances might be present in absorber because of the use of heavy oil for the start-up burners.

**Table 2**  
Summary of Analytical Methods for solid WFGD Absorber Samples.

Analyte – Solid Samples	Method	Reference document	Range
Mercury	Cold Vapor Atomic Absorption Spectroscopy (CVAAS) and amalgamation technique	SC-1.PB.23 Edition 7 from 09.01.2018	0.01–20 mg/kg
As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Zn	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	PN-EN 13657:2006	Se 2–100,000 mg/kg Others: 1–100,000 mg/kg > 100 mg/kg
Al, Ca, Fe, K, Mg, Na, P, S, Si	Wavelength Dispersive X-ray Fluorescence Spectrometry (XRF)	non-pattern method	> 100 mg/kg
Br	Wavelength Dispersive X-ray Fluorescence Spectrometry (XRF)	Internal procedure	> 1 ppm

Uncertainty of the assay – extended, extension factor  $k = 2$ , trust level 95%.

Al, Ca, Fe, Mg, Mn and Si converted to content  $Al_2O_3$ , CaO,  $Fe_2O_3$ , MgO, MnO,  $SiO_2$  in sample.

than the inlet flue gas ( $Hg^{2+} = 4.7 \mu g/m^3$ ). 30–40% of total outlet mercury concentrations left the scrubber in the elemental form  $Hg^0$ . The above situation is unusual for WFGDs units. Moreover, mercury found in the solid phase WFGD slurry was  $Hg = 10 \mu g/g$  (10 ppm) and  $Hg = 1 \mu g/l$  (1 ppb) in the liquor phase.

The mercury found in very high concentrations in the WFGD solids by-product is surprising and uncommon, because the oxidised form of

mercury ( $Hg^{2+}$ ) should be completely soluble in most WFGD liquors [1–3]. A similar observation was made by EPRI [1] in their projects on evaluating the fate of mercury in the WFGD systems. Their analysis of the WFGD by-products showed that the solid phase mercury concentrations were in the range of < 0.1 to nearly 1 ppm, while liquor concentrations were typically 1 ppb or less. They also were partially surprised, because they predicted that the oxidised form of mercury

**Table 3**  
Summary of Analytical Methods for liquid WFGD Absorber Samples.

Analyte – Liquid Samples	Method	Reference document	Range
Mercury	Cold Vapor Atomic Absorption Spectroscopy (CVAAS) and amalgamation technique	PN-EN ISO 12846:2012 + Ap1:2016-07 US EPA 7473	0.00005–10 mg/l 0.05–10000 $\mu g/l$
metals and non-metals	Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)	PN-EN ISO 11885:2009	Ca 0.0010–1000 mmol/l, 0.020–20000 mg/l Mg 0.0010–1000 mmol/l, 0.012–12200 mg/l Na 0.0010–5000 mmol/l, 0.023–115000 mg/l K 0.0010–1000 mmol/l, 0.039–39100 mg/l Li 0.0010–1000 mg/l, 0.00015–144 mmol/l; Ba 0.0002–2000 mg/l, 0.000003–29.1 mmol/l Sr 0.0002–1000 mg/l, 0.000005–22.8 mmol/l Fe 0.0005–1000 mg/l 0.00002–35.8 mmol/l Mn 0.0002–1000 mg/l, 0.000008–36.4 mmol/l Cd 0.0002–1000 mg/l Cr 0.0005–1000 mg/l Co Zr 0.0010–1000 mg/l V 0.0005–1000 mg/l Cu Mo Ni 0.0020–1000 mg/l B Pb Zn 0.0050–1000 mg/l, Al 0.010–1000 mg/l Sb 0.0020–1000 mg/l Ag As Se Sn 0.0050–1000 mg/l Bi 0.010–1000 mg/l Sog. 0.05–10000 mg/l $SO_4^{2-}$ 0.001–208 mmol/l $SO_4^{2-}$ 0.017–3330 mg/l S Si og. 0.050–100 mg/l; $SiO_3^{2-}$ 0.0013–2.63 mmol/l, $SiO_3^{2-}$ 0.040–80 mg/l; $SiO_2$ 0.020–44 mg/l Si P og. 0.010–5000 mg/l; $PO_4$ 3–0.0003–158 mmol/l; $PO_4^{3-}$ 0.003–1630 mg/l; P 0.007–3740 mg/l $P_2O_5$ 0.40–250 mg/l, 0.0032–1.97 mmol/l Chlorides 0.0080–5000 mmol/l, 0.28–177300 mg/l Sulfates 0.0020–208 mmol/l 0.10–10000 mg/l Iodides 0.0024–1.97 mmol/l, 0.30–250 mg/l nitrates 0.00030–17.7 mmol/l 0.020–1100 mg/l 0.0045–249 mg/l N 0.006–100 mg/l $NO_2$ 0.00013–2.17 mmol/l 0.0018–30.4 mg/l N Bromates 0.0030–1.0 mg/l 3.0–1000 $\mu g/l$ 0.0032–3.79 mmol/l 0.10–120 mg/l 0.033–39.1 mg/l P 0.50–500 mg/l
Iodides	Titration	SC-2.PB.07.29 ed. 3 z dn. 02.01.2013	
Inorganic anions – Chlorides	Ion chromatography (IC)	PN-EN ISO 10304–1:2009	
Inorganic anions – Sulfates	Ion chromatography (IC)	PN-EN ISO 10304–1:2009	
Inorganic anions – Iodides	Ion chromatography (IC)	PN-EN ISO 10304–3:2001 chapter. 4	
Inorganic anions – Nitrates	Ion chromatography (IC)	PN-EN ISO 10304–1:2009	
Nitrites	spectrophotometric	PN-EN 26777:1999	
Bromates	Ion chromatography (IC)	PN-EN ISO 15061:2003	
Phosphates	Ion chromatography (IC)	PN-EN ISO 10304–1:2009	
Sulfites	Flow injection analysis (FIA) with spectrophotometric detection	SC-2.PB.07.54 ed. 1 from. 10.01.2013	

**Table 4**  
WFGD Solids Chemical Characterization.

Element/compound	Concentration [% wt. (%m/m)] [dry basis]	Element/compound	Concentration [mg/kg (ppm)] [dry basis]
Al	2.45	As	19
Al <sub>2</sub> O <sub>3</sub> (from conversion)	4.63	Br	< 1
Ca	17.9	Cd	< 1
CaO (from conversion)	25.0	Co	8
Fe	1.81	Cr	74
Fe <sub>2</sub> O <sub>3</sub> (from conversion)	2.59	Cu	34
K	0.86	Hg	10
Mg	2.07	Mn	527
MgO (from conversion)	3.43	MnO (from conversion)	680
Na	0.13	Mo	5
P	0.43	Ni	39
S	12.7	Pb	51
Cl	0.04	Sb	< 2
Si	5.2	Se	84
SiO <sub>2</sub> (from conversion)	11.2	Sr	153
		Zn	73

**Table 5**  
Mineral composition – Diffractometry – X-ray Diffraction (XRD).

Component	Concentration, %
Gypsum (CaSO <sub>4</sub> ·2H <sub>2</sub> O)	75–77
Quartz (SiO <sub>2</sub> )	6–7
Feldspar (K[AlSi <sub>3</sub> O <sub>8</sub> ], Na[AlSi <sub>3</sub> O <sub>8</sub> ], Ca[Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ])	2–4
Calcite (CaCO <sub>3</sub> )	1–2
Illite + muscovite (KAl <sub>2</sub> [AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> ])	< 1–2
Amorphous substance	11–12

\*Potassium feldspar– K[AlSi<sub>3</sub>O<sub>8</sub>].\*\* plagioclase – Na[AlSi<sub>3</sub>O<sub>8</sub>] (albite) – Ca[Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>] (anorthite).**Table 6**  
Liquid phase of slurry chemical characterization.

ions	mg/l	ions	mg/l
nitrites	< 1	phosphates	0.025
nitrites	< 0.02	Organic phosphorus	0,1
bromides	34	iodides	130
chlorides	2390	Sulfates (SO <sub>4</sub> <sup>2-</sup> )	23,500
fluorides	110	sulfides	< 0.5
bromates	< 0.2	sulfites (SO <sub>3</sub> <sup>2-</sup> )	< 0.4
chlorates	< 2	boron	230
chlorites	< 2	RWO	160
Σ chlorates + chlorites	< 4	N org.	130
Mg	7420	Zn	1.6
K	285	Al	< 0.1
Na	3360	Cd	0.060
Sr	2.9	Co	1.34
Ca	593	Cu	0.068
Mn	644	Mo	< 0.02
Fe	0.018	Ni	2.45
Sb	< 0.02	Pb	0.081
As	0.069	Se	1.5
Cr	< 0.03	Hg	0.001

**Table 7**  
Changes of pH, redox potential and temperature during measurements.

Sampling	pH,	Redox, mV	T, °C
1	5.03	280.5	59.6
2	5.04	281.6	59.1
3	5.04	279.3	58.7

**Table 8**  
Lignite characterization.

parameter	unit	lower limit calorific value	Warranty average	upper limit calorific value
Q <sub>it</sub> <sup>f</sup>	MJ/kg	8.5	9.75	11.0
W <sub>t</sub> <sup>r</sup>	%	31	31	34
A <sub>t</sub> <sup>d</sup>	%	46	41	35
S <sub>t</sub> <sup>d</sup>	%	2.8	3.0	max. 3.5
Flammable composition				
C	%	63.0	64.76	67.0
H	%	5.6	5.71	6.1
N	%	1.5	1.18	1.5
O	%	24.9	23.45	20.2
S <sub>daf</sub>	%	5.0	4.9	5.2
sum		100	100	100

Content of volatile combustible V<sup>daf</sup> 53,38%.

Fe content in lignite – 20 g/kg.

Ask melting T<sub>a</sub>, T<sub>b</sub>, T<sub>c</sub> 1251, > 1500, > 1500 °C.The worst specific sulfur must be considered S<sub>m</sub> 2.2 g/MJ.The content of tar in the flammable T<sub>dafSK</sub> 10.3%.The content of arsenic in dry matter A<sub>sd</sub> 21.9 ppm.Content CO<sub>2</sub> 0.23%.S<sub>t</sub><sup>d</sup> denotes all the sulfur in an anhydrous sample.S<sup>daf</sup> – denotes combustible sulfur in the flammable.**Table 9**  
Lignite characterization - trace element contents.

Element	mg/kg [ppm]	Element	mg/kg [ppm]	Element	mg/kg [ppm]
Ag	3.02	Ga	28.5	Sr	138.47
Ba	335.7	Hg	0.22	Te	0.12
Be	4.87	Mn	151.68	Tl	8.64
Br	27.48	Mo	7.83	U	8.22
Bi	6.86	Nb	34.05	V	179.53
Cd	0.33	Ni	81.96	W	9.09
Cl	176.96	Pb	30.56	Y	47.62
Co	24.94	Rb	171.86	Zn	151.72
Cr	105.89	Sb	0.9	Zr	577.6
Cu	71.06	Se	2.37		
F	291.5	Sn	6.94		

**Table 10**  
Ash chemical analysis.

Component	Share, %	Component	Share, %
SiO <sub>2</sub>	50.24	Na <sub>2</sub> O	0.77
Al <sub>2</sub> O <sub>3</sub>	26.90	K <sub>2</sub> O	1.41
Fe <sub>2</sub> O <sub>3</sub>	13.31	P <sub>2</sub> O <sub>5</sub>	0.46
CaO	2.53	TiO <sub>2</sub>	1.22
MnO	0.04	SO <sub>3</sub>	1.57
MgO	1.28		

should be soluble in the WFGD liquid. That is, aqueous equilibrium predicts that Hg<sup>2+</sup> salts that could form with most WFGD anions (e.g., sulphite, sulphate, carbonate and chloride) should be very soluble, and should not precipitate into the solid phase under the WFGD operating conditions [1]. The EPRI bench-scale WFGD tests conducted with pure compressed SO<sub>2</sub> gas mixtures (i.e., unknown H<sub>2</sub>S content) showed that most of the mercury leaves the bench-scale WFGD system with the solid by-products. The theory is that Hg<sup>2+</sup> might be reduced to less soluble Hg<sup>1+</sup>, which in turn precipitates as salts with the WFGD anions. Still other theories consider that mercury does not precipitate but instead adsorbs on the WFGD by-product solids, particularly on impurities such as fly ash, minerals brought into the system with the WFGD reagent, and/or carbon carryover from the furnace. This theory is supported to some extent by the observation that gypsum fines contain higher mercury concentrations than the large gypsum particles [23,34].

The WFGD impurities tend to be fine particles, and fine particles have a much greater surface-area-to-mass ratio than large particles. Moreover, the fine particles should have a greater mercury adsorption capacity per mass than large, non-porous gypsum crystals. Mercury concentrations tend to be the highest in the WFGD solid by-products from units that fire low-sulphur coal and that generate mostly oxidised mercury in the flue gas, and these conditions produce the highest ratio of mercury absorbed by the WFGD solid by-products [1].

It is also possible that other WFGD species impact the fate of mercury that is absorbed by the WFGD system; therefore, the characterisation of the concentrations of these species may provide insight into the observed behaviour of the absorbed mercury.

WFGD systems are known to remove a high percentage of mercury in the coal flue gases. This raises several questions about the fate of mercury removed by the WFGD: Does the absorbed mercury stay in the WFGD liquor or does it leave with the by-product solids, what parameters are affecting mercury reduction and re-emission from the scrubber the most?

### 3.2. Sulphite ions in the scrubber solution

Sulphur ions (sulphates, sulphites) occur in absorbers in high concentrations and certainly affect the behaviour of mercury. Blythe et al. [4] and Krzyżńska et al. [6] claim that the oxidised form of mercury may be reduced by sulphite ( $\text{SO}_3^{2-}$ ) and bisulphite ( $\text{HSO}_3^-$ ) ions in the scrubber solution. Blythe investigated the effects of temperature, reactant concentrations, pH, chloride, thiosulphate, and other complexing agents on the rates of these reactions, and thus on the re-emission of Hg from the WFGD systems. He found that even fairly low concentrations of chloride have a significant effect on the rate of mercuric ion reduction by sulphite. Evidence was found for the formation of complexes of mercuric ion with both sulphite and up to two chloride ions. Each chloride ion attached to mercury slows the decomposition of the mercuric chloride complex to elemental mercury by a substantial amount. The key role of the sulphite aqueous species ( $\text{SO}_3^{2-}$ ) indicates that other solution components (such as magnesium and calcium) ions, which pair up with sulphite ions, could also influence the kinetics of mercury reduction. The effect of calcium on the re-emission was found to increase with the pH increasing [4].

The effect of pH and sulphite concentration are complex and appreciable, particularly at low sulphite concentrations. Low concentrations of sulphite (consistent with forced oxidation conditions) produces a high re-emission and an unusual pH response: the re-emission increased with the pH increase from 4.0 to 6.0. At higher sulphite concentrations, the re-emission generally decreases with pH increasing. Thiosulphate appears to inhibit the re-emission at a low pH but accelerate it at a high pH. The effect of N-compounds are also mixed; sulphur-nitrogen species in the WFGD liquor (a result of  $\text{NO}_x$  in the scrubbed gas) tend to increase the re-emissions, while  $\text{NO}_x$  in the simulated flue gas (in the absence of sulphur-nitrogen species) tends to lower the re-emissions [4].

Blythe et al. developed a chemical kinetics model to describe the aqueous mercury-sulphite-chloride-thiosulphate system considering the simultaneous occurrence of a number of reaction steps. Their model predicts the basic trends observed experimentally for pH, sulphite, and chloride effects, and offers a reasonably good numerical agreement with their experimental data. It has been used to correlate bench-scale experimental results as well as to predict kinetics in low pH regions, such as at the  $\text{SO}_2$  gas-aqueous interface, which are difficult to investigate experimentally [4]. Their model was based on a set of reactions and on known or measured rate constants. All the pertinent reactions found in the Hg-sulphite kinetics literature were added to his model. The Blythe model [4] implies that the mechanism of reduction proceeds primarily via the chloromercuric sulphite complexes in more acidic solutions. The chloride essentially provides a ceiling to limit the rate of reaction at low pH. According to the Authors mechanism

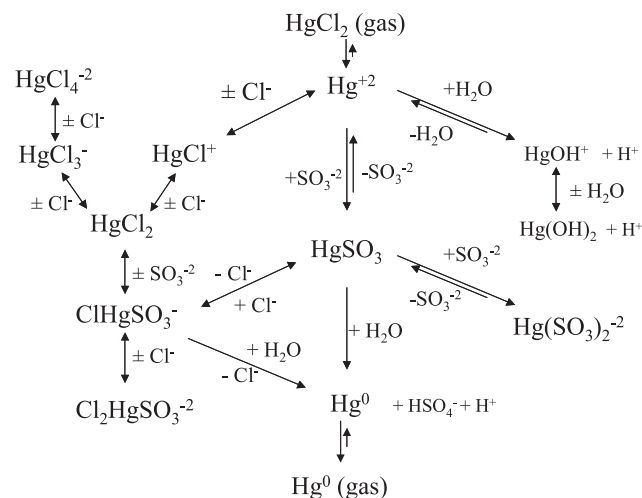
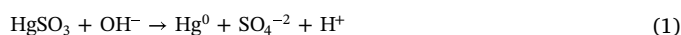


Fig. 1. Schematic Diagram of Main Reaction Pathways in Blythe Kinetics Model. [4]

changes to primarily occur through the mercuric disulphate complex at higher pH. This change of mechanism could explain some of the “complex” behaviour often observed in re-emission results. Even at higher pH the chloromercuric sulphite complexes have a role, because without them the mercuric chloride complexes tend to shut down mercuric reduction completely at approximately the 100 mM (~3500 ppm) chloride level. The model predicts the basic trends experimentally observed for pH and sulphite effects. A simplified schematic depiction of the model reactions is shown in Fig. 1 [4].

Blythe WFGD bench scale testing provided results for a wider range of conditions than could be followed spectroscopically and produced some unexpected results. One of them is an increase in the rate of mercuric reduction at a high pH and low sulphite. A reaction (Eq. (1)) was subsequently added to the kinetics model, which seems to account for this, assuming the catalysis of the mercuric sulphite ( $\text{HgSO}_3$ ) redox reaction under basic conditions.



This is a reasonable reaction that appears to occur in parallel with the usual reaction involving  $\text{H}_2\text{O}$  in place of  $\text{OH}^-$ . That reaction (Eq. (1)) only becomes important in relation to the reaction involving  $\text{H}_2\text{O}$  at an elevated pH (e.g.,  $\text{pH} > 7$ ) [4]. In our cases, such a situation may take place in the region where fresh slurry with a high pH is introduced to the suspension, where sulphite ions can be present. Sulphate ions dominate in the investigated absorber (Table 6).

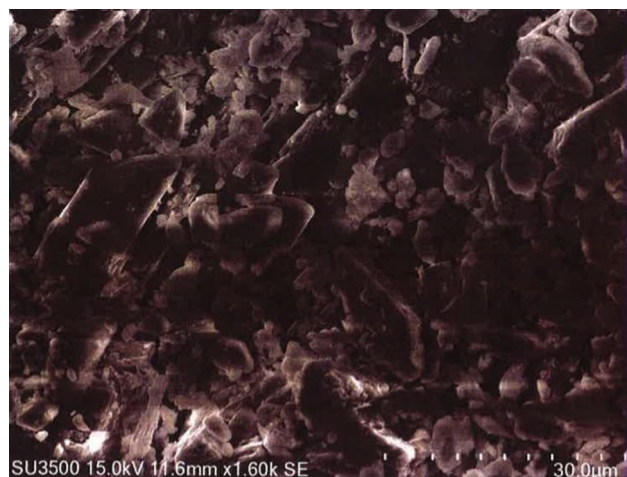


Fig. 2. SEM micrographs of the slurry solid phase – 30 μm.

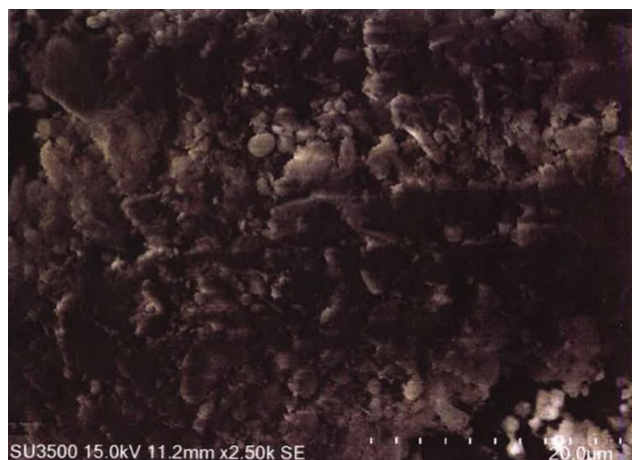


Fig. 3. SEM micrographs of the slurry solid phase – 20  $\mu\text{m}$ .

Blythe et al. [4] developed also a good explanation for the “induction time” behaviour, which they observed in some experiments. There are several possible sources of this behaviour. One of them is the build-up of the elemental mercury product, which could react with mercuric complexes or reaction intermediates. Bulk phase elemental mercury is very insoluble in water (0.3  $\mu\text{M}$  at 25  $^{\circ}\text{C}$ ), but the formation of colloidal mercury is well known in the literature [24,25]. However, they did not observe such a formation visually; colloids are often invisible to the eye. Also, there was some evidence that sulphite was being decomposed at more than stoichiometric amounts in some Blythe runs. If this is true, there is the possibility that mercury catalyses the disproportionation of sulphite, which is thermodynamically favoured but very slow under most conditions. Eq. (2) represents a complete disproportionation of sulphite:



Other reduced sulphur compounds may also be created. These reduced sulphur species could provide a pathway for the fast reduction, which researchers observed after an induction time in some runs. There is also another interesting application. Reports of mercuric sulphide being formed in the WFGD systems are fairly common [31,32], although sulphide is not normally present in WFGD liquors. However, if sulphide was formed via catalysis by mercury, it would be near mercury at a molecular level and could then react with a mercury species to form HgS before being oxidised. HgS is highly insoluble and thus could be separated from the liquid phase reactions as a solid [4,17].

The reaction mechanisms involved in the mercury re-emission proved to be more complex than predicted. Furthermore, new information became available from sampling of the full-scale WFGD systems, which indicates that there is a mechanism whereby mercury is adsorbed on and/or co-precipitated with solids in the WFGD slurry. This mercury phase change will obviously impact the re-emission kinetics. If the  $\text{Hg}^{2+}$  is no longer in the WFGD liquor, it is not available to participate in the aqueous phase reactions. A new integrated re-emission model will have to consider this phase change and how it impacts on the overall re-emission rates. More research is needed to determine the mechanism for this mercury phase change and to develop adsorption and/or co-precipitation rate data as a function of WFGD conditions [4].

### 3.3. Trace elements

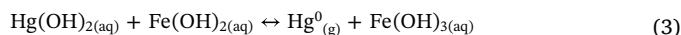
Some researchers investigated other parameters, like trace and major elements contents of the WFGD slurry, as the parameters that affected the fate of mercury [4,13,16,18,20]. There is research showing that minor components from limestone dissolution such as Fe, Sn, Cu, Mn, Ni and Co may reduce the  $\text{Hg}^{2+}$  species [4,13,16,18,20].

Moreover, cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  may form sulphite compounds and, consequently, lower the formation of mercury sulphite species. Similarly, the addition of either fluoride or nitrate ions to the solution decreases the mercury re-emission, possibly because of the formation of stable compounds with  $\text{Hg}^{2+}$  [14]. Blythe et al. [4] found that ions of magnesium and calcium could play role in mercury re-emission. The effect of magnesium and calcium ions is complex, and in accordance with Blythe modelling results it appears that at high sulphite concentrations, magnesium has little effect on re-emission (lowering it somewhat in one run). However, at low sulphite concentration  $\text{Mg}^{2+}$  tends to increase re-emission. This is probably due to the ion pairing of  $\text{Mg}^{2+}$  with  $\text{SO}_3^{2-}$ , which tends to lower the effective sulphite concentration, allowing to accelerate the reduction of mercuric sulphite (and possibly chlorosulphite) complexes. Whereas, the addition of calcium ion to the solution has a larger and more complex effect than anticipated. Blythe et al. [4] did a series of runs with the calcium level set at 15 mM (close to typical WFGD operation) and varied the pH and sulphite concentration. They found that the re-emissions rate increased somewhat with calcium ion addition at a reaction tank pH of 4.0. The effect was much larger at pH 6.0. Results at pH 5.0 were intermediate between those at pH 4.0 and 6.0. The reason for this behaviour is still unclear. It may be that the catalysis of the mercuric reduction reactions by calcium ion or calcium sulphate solids is simply more noticeable at a higher pH, where the reaction is slower, than at the lowest pH where the reactions are already rapid.

Furthermore, other species, such as  $\text{Fe}^{2+}$ , can be oxidised to their higher oxidation states (e.g.,  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ) in the scrubber solution and, consequently, reduce the ionic mercury to elemental mercury. Similar to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$  may reduce the mercury emission because it sequesters sulphite anions by forming ferric sulphite [13,18].

Ochoa-Gonzalez et al. [18] showed that divalent metals, like  $\text{Fe}^{2+}$ , are one of the most important factors in the mercury reduction mechanism. Ochoa-Gonzalez et al. [18] report the impact of limestone characteristics on the mercury re-emission from simulated WFGD slurries prepared from three Spanish limestone samples. To investigate the re-emission of mercury, they performed a series of experiments with gypsum slurries produced by adding sulphuric acid to the limestones. The results show that the  $\text{Hg}^0$  concentration at the outlet of the reactor differed for the gypsum slurries obtained from the different limestones and varied during the tests.

They investigated also the influence of metals such as Fe, mainly in calcium carbonate sorbent, marked CaC (with a high content of Fe (877 ppm), Mn (77 ppm) and Cu (1.2 ppm) which may also have an important role in the mercury re-emission [18]. The protons in the slurry at lower pH values may hinder the formation of  $\text{Fe}(\text{OH})_2$  in the solution preventing the mercury re-emission in accordance with Eq. (3):



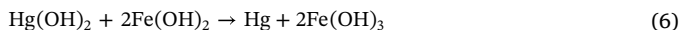
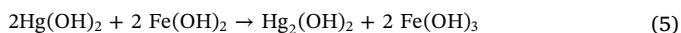
The concentration of Fe in the CaC limestone was the highest among the tested, whereas the gypsum produced by this limestone caused a reduction in  $\text{Hg}^{2+}$  of nearly 100%. An analysis of the produced sludge revealed a significant concentration of Fe for CaC and CaB (1919 and 229 ng/L, respectively) and Mn concentrations of 1010 ng/L for CaB and 1280 ng/L for CaC. Limestone labelled CaB had a much lower concentration of Fe, Mn and Cu (79 ppm Fe, 128 ppm Mn, 0.6 ppm Cu). Thus, the high Mn and Fe concentrations in the sludge of CaC could explain the high degree of  $\text{Hg}^0$  re-emission in the case of this limestone compared to CaB (at pH 6.0). The authors investigated also the effect of the contribution of metals to mercury re-emission in the lab-scale scrubber and investigated without the presence of sulphur species in the reactor [18]. Increasing concentrations of CaC limestone, which produced the highest  $\text{Hg}^0$  vapour pressure, were tested under the same conditions. These results indicated that the mercury reduction increased with high proportions of CaC limestone in the slurry. To confirm the possible influence of divalent and trivalent iron, they

performed a final set of experiments in which  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  were added to CaR gypsum (calcium carbonate reagent – reference material,  $\text{Fe} < 0.1$  ppm,  $\text{Mn} < 0.1$  ppm,  $\text{Cu} < 0.1$  ppm), which did not generate any  $\text{Hg}^0$  re-emission, and to CaC. As expected, the addition of  $\text{Fe}^{2+}$  to the CaC slurry did not modify the  $\text{Hg}^0$  vapour pressure. However, the addition of  $\text{Fe}^{3+}$  delayed the rate of reduction of the  $\text{Hg}^{2+}$  species by modifying the equilibrium of the above-shown reaction and favouring the formation of  $\text{Hg}(\text{OH})_2$  in the slurry. Moreover, the addition of  $\text{Fe}^{2+}$  to the CaR slurry resulted in a significant re-emission of  $\text{Hg}^0$ , whereas the presence of  $\text{Fe}^{3+}$  favoured the formation of a small concentration of  $\text{Hg}^0$  in the flue gas. The addition of  $\text{Fe}^{2+}$  shifted the equilibrium of Eq. (4) to the right, increasing the  $\text{Hg}^0$  vapour pressure, whereas the presence of  $\text{Fe}^{3+}$  may have produced  $\text{Fe}^{2+}$  in the absence of oxygen increasing the  $\text{Hg}^0$  concentration.



For all these reasons, the reduction of  $\text{Hg}^{2+}$  by divalent metals (marked in eq (4) as M) seems to be the most probable pathway for mercury re-emission under these conditions [18].

Similar observation was made by Schütze et al. [13] who claim that iron is reducing soluble  $\text{Hg}^{2+}$  to less soluble  $\text{Hg}^{1+}$  compounds and to certain degree to elemental Hg, according to Eqs. (5) and (6):



The Hg mass balance of their experiment showed that almost 60% was found in the fine particle fraction and 25% emitted. Solubility of  $\text{Hg}^{1+}$  species (e.g. 3.45 mg/l  $\text{Hg}_2\text{Cl}_2$  or 0.785 mg/l  $\text{Hg}_2\text{Br}_2$  at 25 °C) and elemental mercury (0.0562 mg/l  $\text{Hg}^0$  25 °C) is approximately 10–4-fold lower than that of  $\text{Hg}^{2+}$  species [5].

Moreover, research of Ochoa-Gonzalez [18] showed limestone samples with a smaller particle size, higher porosity, and lower magnesium content result in higher reactivity and enhance mercury capture in the scrubbers. A higher mercury re-emission was observed when limestone samples with higher iron contents were tested using a simulated flue gas without oxygen. It follows that plant conditions that fail to provide sufficient aeration to generate  $\text{Fe}^{2+}$  should be avoided to minimize the  $\text{Hg}^0$  re-emission in WFGD systems.

Another interesting research on influence of aluminium (Al) salts on mercury behaviour was performed by Ochoa-Gonzalez et al. [11] They found that in solutions containing sulphite ions, the presence of aluminum sulphate favours the reduction of mercury and that the kinetics of the process depend on the amount of aluminum sulphate and there is a relation between the concentration of aluminum sulphate and the amount of elemental mercury reemitted to the atmosphere. When the concentration of aluminum sulphate reaches 10 mM in the presence of sulphite ions, the reduction of the oxidized mercury species occurs quickly. However, when aluminum sulphate is added in the absence of sulphite ions, the reduction of  $\text{Hg}^{2+}$  does not occur. The use of aluminum sulphate as an additive in the WFGD systems prevents the reduction of mercury and its subsequent re-emission. Aluminum sulphate decreases the pH of the slurry to a level where the sulphite ions, responsible for the mercury reduction, are formed [11]. The correlation between aluminum sulphate and mercury reduction may be due to the presence of aluminum ions in the scrubber solution. The aluminum ions are hydrolysed in aqueous solutions to form hydrated aluminum ( $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ) which generates protons. As a result, the pH decreases and the stability of the mercury in solution is diminished. The role of aluminum in that process was confirmed by various experiments with solutions containing the same quantity of sulphite and adding 10 mM/l of sulphate ions in the form of sodium sulphate instead of aluminum sulphate. No significant differences were observed in mercury behaviour in the presence of sodium sulphate when compared to the blank. In all cases,  $\text{Hg}^{2+}$  dissolved inside the reactor until the concentration reached a value of 0.4 mg/l; the mercury reduction occurs in all cases at

the same speed. In these solutions, the pH decreased during the experiment and the point of reduction was established as taking place at a pH lower than 6.0 [11].

These data prove that the addition of aluminum sulphate in the presence of high sulphite concentrations favours the reduction of  $\text{Hg}^{2+}$  which is due to the decrease in pH, since mercury forms stable complexes with sulphite ions such as  $\text{HgSO}_3$  or  $\text{Hg}(\text{SO}_3)_2^{2-}$  at pH values higher than 6.0. However, it cannot be discarded that the formation of  $\text{Al}^{3+}$  complexes prevents the formation of stable complexes of  $\text{Hg}^{2+}$  in the solution. These findings were verified also in another series of experiments carried out on gypsum slurries [11]. In these experiments, 10 mM of sulphate ions were introduced as aluminum sulphate or sodium sulphate into the reactor containing 100 g of gypsum slurry prepared from natural limestone. When aluminum sulphate was absent in the slurry, most of the oxidised mercury species were reduced to  $\text{Hg}^0$  in a short time, the pH of the suspension being 7.0. The same behaviour was observed in the experiment in which a similar amount of sulphate ions, sodium sulphate, was added to the natural limestone. When sodium sulphate was used in these conditions instead of aluminum sulphate, the reduction of oxidised mercury was detected, as in the case of the aqueous solutions. When in the second test the aluminum additive was incorporated into the reactor, it was observed that the pH of the suspension decreased drastically and that no  $\text{Hg}^{2+}$  was re-emitted. This result suggests that the aluminum additive in their conditions prevented the re-emission of the elemental mercury originating from the reduction of mercury dissolved by the sulphite ions.

It showed, therefore, that aluminum sulphate prevents the re-emission of mercury only if it is added in such a high quantity that it decreases the pH at which no sulphite ions could be formed in the slurry. Moreover, when aluminum sulphate was present in the reactor, either with gypsum or with limestone, mercury was primarily retained in the liquid fraction, since soluble mercury species such as  $\text{HgCl}_2$  were formed [11].

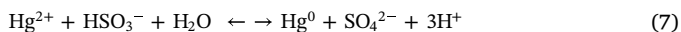
It is worth mentioning that average concentrations of iron in the gypsum from the WFGD in literature are: 758 mg/kg to 0.37% wt. [27], 0.173 – 0.42% wt. [28] Average concentrations of manganese in the gypsum from the WFGD in mg/kg in the literature are: 1.06 – 31.65 [27], 79 – 150 [28], and 2.1 – 56. [29] Average aluminum concentrations in the gypsum from the WFGD in % wt. in the literature are: 0.31 – 1.78 [27], 0.31 – 1.78 [28].

Considering the above data, concentrations of iron, manganese and aluminum found in the investigated samples of the WFGD solids are very high compared to the other scrubbers reported in the literature [27–29]. Concentrations of iron, manganese and aluminum are presented in Tables 4–6 and 9. We believe that iron (Fe), which occurs in very high concentrations in the solid WFGD samples (1.81% wt. Fe), liquid (18 µg/l Fe) and lignite (up to 20 g/kg Fe) is mainly responsible for disrupting the mercury absorption in the scrubber, the partitioning of the mercury between phases and leads to its re-emission.

### 3.4. The pH value and redox potential

The slurry pH is a very important parameter, which can affect mercury capture and its re-emission. However, the effect of pH on the removal/re-emission of mercury in the WFGD systems has still not been fully explained. Some authors have observed a greater retention of mercury at high pH values [11,13,14]. The pH values higher than 7.0 would cause the oxidation of sulphite and bisulphite favouring the reaction between sulphate and mercury species [12]. However, Wu et al. have observed the opposite effect in suspensions containing calcium sulphite [9]. Moreover, Schuetze et al. studies at a laboratory scale concerned the addition of calcium carbonate to facilitate the pH control [13]. According to some research, there is evidence that increasing the pH causes the increase in mercury re-emission [8,6,13]. For example, Chen et al. [8] performed six tests at different initial pH values (3.0, 4.0, 5.0, 5.5, 6.0 and 7.0) in the simulated scrubber ( $\text{CaCO}_3$  slurry,

55 °C). They observed that  $\text{Hg}^0$  concentration in the flue gas reached about  $5.60 \mu\text{g}/\text{m}^3$  at  $\text{pH} = 7$ , 100 min. and only  $2.09 \mu\text{g}/\text{m}^3$  was obtained for  $\text{pH} = 3$ . The Eq. (7) was a reversible reaction, to the principle of chemical reactions, and a counter reaction was performed at a lower pH value, where the concentration of  $\text{H}^+$  was high [8].



Therefore,  $\text{Hg}^0$  re-emission rate decreased in the solution as the pH value decreased. Similar observation was made by Wu et al. [9]. Mercury re-emission rates increased as the slurry's pH values increased (examined pH 4.5, 5.0, 6.0, 6.5 at 50 °C,  $\text{CaCO}_3$  slurry), and the  $\text{Hg}^0$  re-emission rate was smallest when the pH of the slurry was 4.0 [9]. Those experimental results are informative, but we have to remember that the optimal pH of the slurry is about 5.5 for  $\text{SO}_2$  removal and decreasing it can decrease the  $\text{SO}_2$  removal efficiency and cause additional corrosion problems in real full-scale installations.

From Heidel and Klein research [7], a general conclusion that can be drawn is that for each individual slurry,  $\text{Hg}^0$  re-emission decreases for the increasing redox potential. However, actual redox potentials and Hg re-emission ranges of the slurries differ significantly due to the presence of different halides with individual redox properties [7].

Ochoa-Gonzalez et al. [18] investigated the oxidation-reduction character of WFGD slurries and claim that slurries (with Eh values ranged from  $-300$  to  $-100$  mV) exhibited the lowest reactivity with sulphur and thus, the redox conditions of these suspensions were the most favourable for reducing mercury. Theoretically, the redox potential, in the investigated absorber slurry, has much higher values (about 280 mV), presented in Table 7, than mentioned above and should not be favourable to reducing mercury. Despite that, elemental mercury and its oxidised form was emitted from the scrubber in high concentrations. Therefore, the prediction of Hg re-emission based solely on detection of the redox potential without further information is not expedient.

### 3.5. Aeration flux

The effect of oxygen concentration on the mercury re-emission from limestone-gypsum WFGD slurry was researched by Chen et al. [8]. They found that the concentration of oxygen in the flue gas strongly affects the mercury re-emission. The experiments were performed at a pH of 5.5 and a temperature of 55 °C with the range of oxygen concentration from 0 to 15%. It was discovered that  $\text{Hg}^0$  re-emission rates increase as the oxygen concentration in the flue gas decreases. The  $\text{Hg}^0$  concentration in the flue gas reached about  $6.87 \mu\text{g}/\text{m}^3$  for 0%  $\text{O}_2$  at 100 min., when the  $\text{Hg}^0$  concentration was stable. Conversely, only  $2.62 \mu\text{g}/\text{m}^3$  was obtained for 15%  $\text{O}_2$ . Wu et al. [9] performed a similar experiment with a different oxygen concentration in the flue gas (0, 6, 14, 20.9%). Other operational conditions included a pH value of 6.0, 0.5%wt  $\text{CaSO}_3$  and a slurry temperature of 60 °C. They found, like Chen et al. [8] that  $\text{Hg}^0$  re-emission rates decreased as the  $\text{O}_2$  concentrations increased. They suggest that  $\text{SO}_3^{2-}$  was oxidised to  $\text{SO}_4^{2-}$  when the carrier gas that contained  $\text{O}_2$  was blown into the scrubber according to the chemical reaction in Eq. (8):



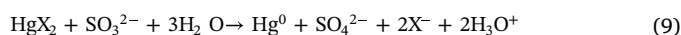
Thus, the concentration of  $\text{HSO}_3^-$  decreased, which resulted in a lower  $\text{Hg}^0$  re-emission rate [9]. The  $\text{Hg}^0$  re-emission reaction mechanism is explained using the chemical reaction in Eqs. (7) and (8).

Moreover, Chen et al. [8] claim that mercury partitioning in the by-products indicates that an increase in mercury retention in the solid fraction occurs at lower concentrations of  $\text{O}_2$  in the flue gas (90% in solid fraction with no  $\text{O}_2$  in the flue gas and about 55% in the solid fraction when  $\text{O}_2$  was 15%). Some authors suggest that sulphate ions may be contributing to the formation of a small amount of mercury sulphate, which then precipitate with the gypsum particles or decomposes in  $\text{HgO}(\text{s})$  [8,10]. However, according to the other researchers

sulphates do not affect mercury much and sulphite ions and sulphites ions ( $\text{SO}_3^{2-}$ ) are the most crucial parameter affecting mercury re-emission [4].

### 3.6. Halide concentration and mixed halide systems ( $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ )

For typical WFGD slurries in coal-fired power plants,  $\text{Cl}^-$  constitutes the majority of dissolved halides. For such slurries, total mercury ( $\text{Hg}^T$ ) re-emission mainly consists of  $\text{Hg}^0$ . Therefore, to avoid or minimize mercury re-emissions, the emphasis should be put on the prevention of reducing conditions, indicated by low redox potentials. Such reducing conditions can result from high  $\text{SO}_3^{2-}$  concentrations due to an insufficient aeration or by increased reducing strength at increased pH-values. However, the prediction of Hg re-emission based solely on the detection of the redox potential without further information is not expedient. Heidel et al. [7] investigated the re-emission of both  $\text{Hg}^0$  and  $\text{HgX}_2$  compounds and illuminated the impact of the halides  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  on the  $\text{HgX}_2$  re-emission mechanism. The compounds  $\text{HgCl}_2$ ,  $\text{HgBr}_2$  and  $\text{HgI}_2$  were characterized by covalent bonds. Covalent characteristic and volatility of the individual  $\text{HgX}_2$ -compounds ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) increased in the order  $\text{Cl} < \text{Br} < \text{I}$  [7,19]. If multiple ligands are present in the solution, several dissolved  $\text{HgX}_2^-$  compounds coexist due to ligand exchange reactions, Eq. (9):



They also performed experiments with slurries containing individual halides of  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$  at different concentration levels as well as with slurries containing multiple halide types [7]. They observed that for all halides considered, the re-emission of  $\text{Hg}^0$  decreased with increasing halide concentration. This can be explained by the shift in complex formation equilibrium to the side of the less reactive compounds  $[\text{HgX}_3]^-$  and  $[\text{HgX}_4]^{2-}$ . For identical halide concentration,  $\text{Hg}^0$  re-emission increases according to the sequence of standard electrode potentials in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ . It must be mentioned, that in all their experiments equivalent stationary concentrations of  $\text{SO}_3^{2-}$  ions was present in the slurry and could react with mercury compounds. Thereby, the formation of heteroleptic and homoleptic mercurate-complexes with  $\text{SO}_2^{3-}$  ligands according to individual ligand concentrations were likely. Authors imply that  $\text{SO}_2^{3-}$  concentrations were also comparable in all experiments, since the  $\text{SO}_2$  removal efficiency and aeration flow rates of the experiments were almost identical. Moreover, the differences in the re-emission of both  $\text{Hg}^0$  and  $\text{HgX}_2$  can be attributed directly to the impact of the individual halides. The desorption of  $\text{HgSO}_3$  into the gas phase can be ruled out due to the absence of  $\text{Hg}^{2+}$  species in the clean gas of slurries containing solely the Cl-halide. Hence, it can be concluded that  $\text{HgBr}_2$  and  $\text{HgI}_2$  are the major  $\text{Hg}^{2+}$  species which are re-emitted in the experiments [7]. It is worth noticing at the point that the iodine ions concentration in the investigated scrubber liquor was 130 mg/l and was higher than that of bromides (34 mg/l). However, usually the iodine concentrations in coal are typically smaller than that of bromine. We have a few theories about why this is happening, but without in-depth research in that direction, all our explanations would be treated as an over-interpretation. One of the theories is a very high concentration of Fe-Mn oxides [30] with which iodine can be linked. Another theory is that additional salts come from the process water used for limestone slurry preparation, but in our opinion this is less likely. The process water is wastewater from the cooling system of a power plant. Chemical composition of wastewater is presented in Table 11 and it is added to the annex of the manuscript. The iodine ion concentration was not measured in the process water, but we plan to do that in the future research. It should be also mentioned that slurries containing  $\text{I}^-$  at relevant concentrations and redox reactions of  $\text{Hg}^{2+}$  compounds have a minor role in the mercury re-emission mechanism. This is due to the very low reactivity and large formation constant of  $[\text{HgI}_4]^{2-}$ . However, due to its high volatility, even small concentrations of  $\text{HgI}_2$  in the liquid phase can lead



**Table 11**  
Chemical composition of wastewater.

	Parameter	Unit	Min	Max
1	CHSK Cr	mg/l	27.1	29.1
2	CHSK Mn	mg/l	4.9	5.3
3	Soluble solids	mg/l	971.9	1049.8
4	Cl <sup>-</sup>	mg/l	100.1	107.6
5	SO <sub>4</sub> <sup>2-</sup>	mg/l	384.5	413.0
6	Ca <sup>2+</sup>	mg/l	99.5	106.8
7	NO <sub>3</sub> <sup>-</sup>	mg/l	33.3	35.8
8	Fe	mg/l	0.0	0.0
9	SiO <sub>2</sub>	mg/l	52.4	563
10	Suspended solids	mg/l	5.4	5.8

to its re-emission into the gas phase. The mechanism of the HgX<sub>2</sub> re-emission is particularly important for low total halide content, relevant I<sup>-</sup> concentration and high temperatures. Formation constants, reactivity and volatility of Hg<sup>2+</sup> species with Br- ligands have a middle position in this comparison. Consequently, HgBr<sub>2</sub> is less reactive than HgCl<sub>2</sub> but simultaneously less volatile than HgI<sub>2</sub>. The lowest Hg<sup>T</sup> re-emission was measured for the slurry containing high concentrations of Cl<sup>-</sup> and Br<sup>-</sup> in the absence of I<sup>-</sup> [7].

### 3.7. Effect of NO

The role of NO<sub>x</sub> in the flue gas stream and resulting nitrogen compounds in the WFGD liquor is of interest, especially since these species add another oxidation/reduction component. NO<sub>x</sub> concentrations in the flue gas and nitrogen compound concentrations in the WFGD liquor can vary strongly depending on whether the boiler has an SCR in service upstream of the WFGD system [4,15]. According to Blythe et al. research [4], the addition of NO<sub>x</sub> to the gas stream produces lower than normal re-emissions. A similar inhibition by NO<sub>x</sub> in the gas was observed in the presence of 15 mM Ca<sup>2+</sup> (typical Ca ions concentration in the WFGD). The addition of nitrite, the aqueous anion formed from the absorption of NO<sub>x</sub> species in a wet scrubber, in the initial sorbent solution also appeared to inhibit the re-emissions to some extent. However, NO<sub>x</sub> in the WFGD inlet flue gas can lead to the formation of sulphur-nitrogen compounds over time, due to a series of reactions that begin with a reaction between nitrite and sulphite. Some sulphur-nitrogen species are known to be reducing species and may influence the mercury re-emissions too [4].

### 3.8. The mercury-binding phase in the WFGD gypsum

Schroeder and Kairies [21] performed settling and dissolution experiments to isolate the material responsible for the strong Hg-gypsum binding. Settling experiments have been partially successful in concentrating the Hg in a slower-precipitating fraction. They found that the Hg was always more concentrated in the top-most, slower-settling layer of the gypsum. This layer was also more brownish in colour, whereas the majority of the gypsum was white. The top layers still contained mostly gypsum but were enriched in Si (8.3%), Al (2.4%), Fe (1.9%) and Mg (1.8%). The top layers were also enriched in the trace metals Ba, Mn, and Ti in addition to Hg. Thus, the strong adsorption observed for Hg may not be specific for this element but a more general phenomenon [21].

Mercury captured in some WFGD gypsums is bound tightly and is not easily removed by thermal or acid leaching processes. The phase responsible for this behaviour appears to be an iron- or iron/aluminum-rich material. Reports on the partitioning of Hg in the WFGD sludge have differed in the distribution of Hg between the aqueous and solid phases. In one case, Hg was accounted exclusively to the fine, rather than crystalline, portion of the solid gypsum. Investigated solid phase of spent slurry mainly consists of gypsum 75–77% (Table 5) and 11–12%

is an amorphous substance. SEM micrographs (Figs. 2 and 3) showed that gypsum from the slurry was composed of small, irregular shapes. According to sample characteristics such morphological structure favors mercury capture. In another, Hg was found to be about evenly distributed between the gypsum and the recycled water. The presence of, what appears to be, a naturally occurring adsorptive phase in some WFGD gypsums may explain the different results observed for different systems [22].

## 4. Conclusions

A very high mercury emission (Hg<sup>0</sup> and Hg<sup>2+</sup>) was observed from the WFGD limestone lignite-fired power station, with a total WFGD flue gas capacity ~1 000 000 Nm<sup>3</sup>/h. The mercury (Hg<sup>T</sup>) concentration in the flue gas at the inlet of the WFGD was 31.4 µg/m<sup>3</sup>, and 21–25 µg/m<sup>3</sup> at its outlet. It was noted that 67–80% of the total inlet mercury concentration left the WFGD scrubber. Moreover, the oxidised form of mercury was the main form of emitted mercury (about 60–70% of the total outlet WFGD mercury concentration), and 30–40% of mercury emitted from the scrubber was in the elemental form. The analysis of the absorber slurry showed that a very high concentration of mercury exists in the solid phase of the spent slurry (10 µg/g), whereas the liquid phase contains just 1 µg/l. This is in line with the EPRI research projects, where the WFGD systems samples were analysed. The mercury re-emission can be caused by many factors, but we believe that iron (Fe), which occurs in very high concentrations in the solid WFGD samples (1.81% wt. Fe.), liquid (18 µg/l Fe) and lignite (up to 20 g/kg Fe) is mainly responsible for disrupting the mercury absorption in the scrubber, the partitioning of the mercury between phases and leads to its re-emission. The fraction of mercury retained in the solid phase of spent slurry probably due to the adsorption of mercury onto the Fe (OH)<sub>3</sub> and gypsum particles. Moreover, Fe in the bivalent oxidation state is one of the components of the WFGD liquor that may transfer the dissolved Hg into the particle-bound form. The bivalent iron causes a marked decrease of the oxidation-reduction potential. This is in line with the reducing properties of this iron species. Mercury can adsorb also on WFGD by-product solids, particularly on impurities such as fly ash, minerals brought into the system with the WFGD reagent, and/or carbon carryover from the furnace.

According to the literature, the concentration of sulphite ions (SO<sub>3</sub><sup>2-</sup>) is the most crucial parameter affecting mercury re-emission. Sulphates do not affect mercury much. Our ion liquid analysis of spent slurry showed a low sulphite (SO<sub>3</sub><sup>2-</sup>) ion concentration (below 0.4 mg/l), whereas the sulphate (SO<sub>4</sub><sup>2-</sup>) ion concentration was very high: 23 500 mg/l. That means that almost all sulphites were oxidised to sulphates. They were oxidised during the aeration process. Sulphites could exist in the absorber in higher concentrations and could contribute to the mercury re-emission mechanism too. Even that small concentration of sulphites may be enough for reducing the micrograms of dissolved mercury.

The ion liquid analysis of spent slurry showed a high concentration of chlorine ions (2390 mg/l) and relatively high quantity of iodine ions (130 mg/l). Some research indicates that dissolved oxidised mercury may have a fairly high vapour pressure in water as long as no complexes, such as HgX<sub>3</sub><sup>-</sup> and HgX<sub>4</sub><sup>2-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>), are formed. Especially HgI<sub>2</sub> is highly volatile. This can also increase the percentage of oxidised mercury (Hg<sup>2+</sup>) concentration in the flue gas at the outlet. In our case, the Hg<sup>2+</sup> at the outlet was ≅ 60–70%. We believe that a relatively high iodine ion concentration (130 mg/l) in the investigated limestone slurry leads to the mercury emission in the oxidised form, mainly as HgI<sub>2</sub>, which is highly volatile. Other minor components from the limestone dissolution such as Mn, Al and Mg may additionally enhance that “complex” mercury behaviour. Considering the re-emission of Hg<sup>2+</sup>, special attention should be placed on the prevention of the formulation of HgI<sub>2</sub> at a significant concentration.

The analysed chemical composition of slurry is favourable to the

mercury re-emission mechanism. To minimise the mercury re-emission, several actions must be taken. One of the first improvement actions could be providing sufficient oxidation – for the best result, before its reductive effect and lowering the redox potential, another is avoiding the pH-driven Hg re-emission (above pH 7.0 in the region where the fresh slurry with a high pH is introduced into the suspension) or the stabilization of  $\text{Hg}^{2+}$  in the liquor phase of the slurry and prevention of the formulation of volatile  $\text{HgI}_2$ .

The presented example shows also that there is a necessity to characterise in detail the chemical conditions in the WFGD system and the flue gas to avoid unnecessary and costly full-scale tests before applying any mercury control technology which is based on chemical reactions. Under the presented conditions, most of them would not work.

#### CRedit authorship contribution statement

**Renata Krzyżyńska:** Conceptualization, Investigation, Formal analysis, Writing - review & editing. **Zbyszek Szeliga:** Resources. **Lukas Pilar:** Resources, Investigation. **Karel Borovec:** Methodology. **Paweł Regucki:** Visualization.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### References

- [1] EPRI Technical Report: The Fate of Mercury Absorbed in Flue Gas Desulfurization (FGD) Systems, 2005.
- [2] EPRI Technical Report. An Assessment of Mercury Emissions from Coal-Fired Power Plants. Palo Alto, CA: EPRI; 2000.
- [3] Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, et al. Status review of mercury control options for coal-fired power plants. *Fuel Process Technol* 2003;82(2–3):89–165.
- [4] Blythe GM, Currie J, DeBerry DW. Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, report 2008.
- [5] Blythe GM, Richardson M, Dene C, Rhudy R, Nolan P. Field study of Mercury Partitioning and Re-emission in Wet-FGD Systems. In Proceedings of 8th Power Plant Air Pollutant Control Mega symposium, Baltimore MD, Aug 30-Sep 2, 2010, Vol. 1; Air and Waste Management Association: Pittsburgh, PA, 2010, pp. 1825–1844.
- [6] Krzyżyńska R, Hutson ND, Zhao Y, Szeliga Z, Regucki P. Mercury removal and its fate in oxidant enhanced wet flue gas desulfurization slurry. *Fuel* 2018;211:876–82.
- [7] Heidel B, Klein B. Reemission of elemental mercury and mercury halides in wet flue gas desulfurization. *Int J Coal Geol* 2017;170:28–34.
- [8] Chen C, Liu S, Gao Y, Liu Y. Investigation on Mercury Reemission from Limestone-Gypsum Wet Flue Gas Desulfurization Slurry. Hindawi Publishing Corporation The Scientific World Journal, 2014, Vol. 2014.
- [9] Cheng-Li Wu, Yan C, Cheng-Chun H, Zhong-Bing D, Wei-Ping P. Study of Elemental Mercury Re-emission through a Lab-scale Simulated Scrubber. *Fuel* 2010;89:2072–80.
- [10] Ochoa-Gonzalez R, Diaz-Somoano M, Martinez-Tarazona MR, et al. Control of  $\text{Hg}^0$  Re-emission from Gypsum Slurries by Means of Additives in Typical Wet Scrubber Conditions. *Fuel* 2013;105:112–8.
- [11] Ochoa Gonzalez R, Diaz-Somoano M, Lopez Anton MA, Martinez-Tarazona MR. Effect of Adding Aluminum Salts to Wet FGD Systems upon the Stabilization of Mercury. *Fuel* 2012;96:568–71.
- [12] Diaz-Somoano M, Unterberger S, Hein KRG. Mercury Emission Control in Coal-fired Plants: The Role of Wet Scrubbers. *Fuel Process Technol* 2007;88:259–63.
- [13] Schuetze J, Kunth D, Weissbach S, Koester H. Mercury vapor pressure of flue gas desulfurization scrubber suspensions: effects of the pH level, gypsum and iron. *Environ Sci Technol* 2012;46:3008–13.
- [14] Wo J, Zhang M, Cheng X, Zhong X, Xu J, Xu X.  $\text{Hg}^{2+}$  Reduction and Re-emission from Simulated Wet Flue Gas Desulfurization Liquors. *J Hazard Mater* 2009;172:1106–10.
- [15] Heijnesson-Hultén A, Nilsson P, Samuelsson M, Ajdari S, Normann F, Andersson K. First evaluation of a multicomponent flue gas cleaning concept using chlorine dioxide gas – Experiments on chemistry and process performance. *Fuel* 2017;210:885–91.
- [16] Ghorishi B, Downs B, Renninger, S. Role of Sulfides in the Sequestration of Mercury by Wet Scrubbers. In: Proceedings of the 31st international coal utilization and fuel system conference, Clearwater, Baltimore, Maryland, USA, 2006.
- [17] Ghorishi B. Role of Sulfides in the Sequestration of Mercury by B&W Wet Scrubbers. OLI User Conference, Morristown, NJ, USA, 2007.
- [18] Ochoa-Gonzalez R, Diaz-Somoano M, Martinez-Tarazona M. Influence of Limestone Characteristics on Mercury Re-emission in WFGD Systems. *Environ Sci Technol* 2013;47(6):2974–81.
- [19] Fleming I. Molecular Orbitals and Organic Chemical Reactions. Reference Ed. XII. Wiley, Hoboken, N.J., 2010, pp. 515.
- [20] Inoue Y, Munemori M. Coprecipitation of Mercury (II) with Iron (III) Hydroxide. *Environ Sci Technol* 1979;13:443–5.
- [21] Schroeder K, Kairies C. Distribution of Mercury in FGD Byproducts, 2005 World of Coal Ash (WOCA), April 11–15, 2005, Lexington, Kentucky, USA.
- [22] Hein KRG, Unterberger S. Status and Prospects of Air Toxic Emissions Reduction Technologies for Coal-Fired Power Plants in Europe. Glasgow, Scotland: Mercury Experts Conference; 2004.
- [23] Babcock & Wilcox Co. And McDermott Technology, Inc., Full-Scale Testing Of Enhanced Mercury Control Technologies For Wet FGD Systems, Final Report, DE-FC26-00NT41006, Babcock & Wilcox Co. And McDermott Technology, Inc. May 7, 2003.
- [24] Wang Q, Qin W, Chai L, Li Q. Understanding the formation of colloidal mercury in acidic wastewater with high concentration of chloride ions by electrocapillary curves. *Environ Sci Pollut Res Int* 2014;21(5):3866–72.
- [25] Raposo RR, Meléndez-Heviab E, Spiroc M. Autocatalytic formation of colloidal mercury in the redox reaction between  $\text{Hg}^{2+}$  and  $\text{Fe}^{2+}$  and between  $\text{Hg}_2^{2+}$  and  $\text{Fe}^{2+}$ . *J Mol Catal A-Chem* 2000;164(1–2):49–59.
- [26] Diao X, Yuan Ch-G, Wua J, Zhanga K, Zhanga Ch, Guia B. Mercury fractions in gypsum and estimation of mercury emission from coal-fired power plants. *Fuel* 2018;226:298–306.
- [27] Sun M, Hou J, Cheng G, Baig SA, Tan L, Xu X. The relationship between speciation and release ability of mercury in flue gas desulfurization (FGD) gypsum. *Fuel* 2014;125:66–72.
- [28] Zhu ZW, Zhuo Y-Q, Fan Y-M, Wang Z-P. Mechanism of mercury vapor release from flue gas desulfurization gypsum. *Fuel Process Technol* 2017;156:485–90.
- [29] Hao Y, Li Q, Pan Y, Liu Z, Wu S, Xu Y, et al. Heavy metals distribution characteristics of FGD gypsum samples from Shanxi province 12 coal-fired power plants and its potential environmental impacts. *Fuel* 2017;209:238–45.
- [30] Peng B-X, Wu D-S. Modes of iodine occurrence in bituminous coal and anthracite and their environmental effects. *J Fuel Chem Technol* 2012;40(3):257–62.
- [31] Sui Z, Zhang Y, Li W, Orndorff, Cao W, Pan W-P. Partitioning effect of mercury content and speciation in gypsum slurry as a function of time. *J Therm Anal Calorim* 2015;119(3):1611–8.
- [32] Renninger SA, Farthing GA, Ghorishi SB, Teets C, Neureuter JA. Using wet FGD systems to absorb mercury. *Power* 2004;148(8):44–9.
- [33] Zhao S, Pudasainee D, Duana Y, Gupta R, Liu M, Lu J. A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. *Prog Energy Combust Sci* 2019;73:26–64.
- [34] Blythe GM, Richardson MK, Steen WA, Dene CE, Nolan PS. Investigation of Mercury Control by Wet FGD Systems. Proceedings of Air Quality VIII Conference. 2011.