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Trace elements retention in bottom ashes during coal combustion with hydrated lime additions

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ABSTRACT

Trace elements (TEs) content in coal, industrial hydrated lime, and bottom ashes from coal combustion and coal with hydrated lime additions were studied in this article. The favorable effect of hydrated lime (HL) addition to coal on TEs retention in ashes was reported for As, B, Co, Li, Mo, and V. However, at the same time, less Cu, Ni, Pb, and Sr were retained in the ash. An experimental studies results was supplemented with thermodynamic equilibrium calculations performed in Factsage software. Based on calculations, it has been shown that addition of HL to coal: (i) reduces formation of liquid slag phase containing, among others, TEs in the following form: $As_2O_3(l)$, $CoO(l)$, $Cu_2O(l)$, $NiO(l)$, $PbO(l)$ and $ZnO(l)$; (ii) favors retaining As, B, Mo, and V in ash, as a result of stable components formation: $Ca_3(AsO_4)_2(s)$, $Ca_3(BO_3)_2(s)$, $CaMoO_4(s)$ and $Ca_3(VO_4)_2(s)$. Interestingly, most of the arsenic in the ash was trapped in $Ba_3(AsO_4)_2(s)$.

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Introduction

Coal-fired power plants are among the major anthropogenic sources responsible for air emissions of such trace elements as Hg, As, Ni and Cr (Environmental Protection Agency U.S., 2018). In the European Union states, air emissions of permissible levels of Hg from large facilities of coal and lignite combustion for energy purposes are regulated by the Industrial Emissions Directive 2010/75/EU (Lecomte et al. 2017). Based on the Best Available Techniques (BAT), the mentioned directive introduces limits of dust emissions, which is equivalent to the reduction of air emissions of trace elements. Based on the EPRTR (The European Pollutant Release and Transfer Register (E-PRTR), 2018) industrial facilities releasing on annual basis over 10 kg Cd, 10 kg Hg, 200 kg Pb are obliged to register emissions of the mentioned trace elements and to prepare annual reports. As it appears from EPRTR, the monitoring of As, Cr, Cu, Ni, and Zn air emissions by industrial facilities in the EU states is not obligatory. Over the period of the last over a dozen years, the emission of trace elements has been significantly reduced by applying modern and clean coal combustion technologies. Reduction of TEs atmospheric emissions has been achieved by installing widely available flue gas cleaning systems, such as flue gas desulphurization plants, electrostatic precipitators, bag filters, cyclones, Duct Sorbent Injection (DSI) and activated carbon systems. In addition, pulverized-coal boilers and fluidized-bed boilers are equipped with installations for sorbent supply to the fuel, or directly to the boiler (Furnace Sorbent Injection). The basic objective for sorbent addition is the reduction of SO_2 emission, via sulfur retention in the ash in the form of $CaSO_4$. In CFB (Circulating Fluidized Bed) furnace desulphurization with limestone is a cost-effective investment, enabling

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achievement of high sulfur removal efficiency of 97% (Yue et al. 2017). What is more, the progress in the research on CFB with ultra-low emission is directed at the elimination of flue gas cleaning systems (Yue et al. 2017). Improvement of the cyclones collection efficiency determines the use of fine sorbent with particle size $< 200 \mu\text{m}$ in modern CFB boilers and $< 1000 \mu\text{m}$ in traditional CFB boilers (Cai et al. 2018). Introduction of sorbent to the combustion chamber can increase the capacity for retaining TEs in fly and bottom ashes. The efficiency of TEs capturing in the combustion chamber is determined by combustion technology and temperature, type of used sorbent, sorbent particle size and mode of TEs occurrence in coal (Contreras and Bahillo 2018; Nalbandian 2012). The basis for efficient sorbent action is proper mixing of sorbent with coal, selection of suitable grain size and ensuring the necessary contact time. Sorbents added to coal combustion chamber exhibit selective impact on TEs retention (Cheng et al. 2001). According to the best knowledge of the authors, the published studies on the influence of sorbent addition to coal boiler on the fate of TEs including the share of added sorbent are scarce (Gullett and Ragnunathan 1994; Wang et al. 2017). The most important conclusions stemming from literature studies on the impact of the addition of various sorbents to coal combustion chamber on TEs retention are listed in Table 1.

The latest research has proven that the efficiency of TEs retention in ash depends on its composition, among others. The highest enhancement in As, Sb and Se retention efficiency has been observed in ashes with increasing Fe_2O_3 content, whereas addition of SiO_2 had an opposite effect (Zhou et al. 2017, 2018). The majority of TEs demonstrate a positive correlation with ash content in coal (Contreras and Bahillo 2018). Although the major source of TEs emission from the combustion behavior is the fuel itself, certain elements are introduced with sorbents (Cotton, Patchigolla, and Oakey 2014; Gullett and Ragnunathan 1994).

The motivation for the present preliminary study is the continuous progress in the development of coal combustion technology in CFB boilers, targeting the addition of sorbents with particle size $< 200 \mu\text{m}$ to combustion chamber. The study objective is to verify whether the application of industrial-hydrated lime as sorbent added to pulverized coal at the rate of 5% and 10% wt. improves the efficiency of trace elements retention in bottom ash. Thermodynamic equilibrium calculations used to forecast forms of TEs occurring in ashes and flue gases constitute a supplement to the experimental results.

Table 1. The influence of various sorbent materials added to the boiler on the capture of trace elements.

Sorbent	Findings	Researchers
limestone	Increased content of CaO in ashes favors retention of As and Br. Decreased retention of Pb, Zn, Ni and Cr demonstrates positive correlation with the ash particle size and their CaO content.	Bartoňová and Klika 2014
kaolinite, bauxite, lime	Kaolinite is the best absorber for Pb, and bauxite for Cd. Kaolinite and bauxite absorb Cr to a minor degree. Addition of calcium does not influence Cr capture.	Cheng et al. 2001
hydrated lime, limestone, kaolinite	Sorbents based on Ca efficiently reduce the concentration of Sb, Hg and Se in sub-microne particles of ash. Kaolinite turned out to be the best absorber for Cd and Pb.	Gullett and Ragnunathan 1994
sand, limestone and aluminum oxide	Calcium is a more efficient absorber than sand and aluminum oxide for capturing lead and cadmium.	Ho et al. 1994
lime	Gaseous As and Se compounds react with CaO forming: $\text{Ca}_3(\text{AsO}_4)_2$ and CaSeO_4 .	Junying et al. 2007
alumina, silica, titania	Aluminum oxide is more efficient in Be and Ni capturing than SiO_2 . On the other hand, TiO_2 and SiO_2 are characterized by high retention degree for Cd and Pb.	Owens, Wu, and Biswas 1999
vanadium pentoxide	V_2O_5 promotes change in the oxidation degree Hg^0 to Hg^{2+} , that is form of mercury which is easily captured.	Wang et al. 2017
Al-, Fe-, Li-, Na-, K-, Be-, Mg-, Ca-based sorbents	Affinity for As adsorption decreases according to this order: $\text{Li} > \text{K} > \text{Na} > \text{Al} > \text{Ca} > \text{Mg} > \text{Fe} > \text{Be}$.	Wu and Barton 2001

Materials and methods

Coal and ash analysis

Pulverized coal from a Polish coal mine was selected for the study. Ultimate and proximate analysis of the coal, ash composition and determination of TEs in coal and ash were performed at the Energopomiar Central Laboratory in Gliwice, Poland. The tests were performed in accordance with standards applicable in Poland: C, H and N (PN-G-04571:1998); total S (PN-G-04584:2001); Cl (DIN 51727:2011); M – total moisture (PN-EN 14774-2:2010); A – ash (PN-ISO 1171:2002); VM – volatile matter (PN-G-04516:1998), FC – fixed carbon (PN-EN15148:2010). On the other hand, TEs in coal and ash composition were examined with the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method with the use of plasma spectrometer Thermo iCAP 6500 Duo ICP.

Hydrated lime analysis

The main components of hydrated lime (HL – acronym used in the further part of the paper) were determined using X-ray diffraction (XRD). For the purpose of XRD tests, a Philips PW1050 apparatus was used, copper lamp with nickel filter, 35 kV/16 mA current, counting time 3 s/position, range $5 \div 65$, step value 0.05 degree 2 theta. In order to determine the HL composition based on the weight loss during its heating, a thermogravimetric analysis (TG/DTG), and Quasi Multiple Ion Detection (QMID) was performed using Netzsch STA Jupiter 449 F3 coupled with Aëolos QMS 403 quadruple mass spectrometer. The major elements contained in HL were determined using Wavelength-Dispersive X-Ray Fluorescence spectrometer (WD-XRF) Axios mAX 4 kW (PANalytical) equipped with an Rh source. The PANalytical standardless analysis package Omnian was applied for quantitative analysis of the spectra. ICP-OES method was used to determine TEs.

Distribution of coal and hydrated lime particle size

The distribution of coal and HL particle size in the range from 0.1 to 600 μm was performed with HORIBA LA-300 granulometric characteristics laser analyzer.

Combustion experiments

Three samples were prepared for the tests: coal; 100% coal + 5% wt. HL and 100% coal +10% wt. HL. The combustion was realized in a laboratory tube furnace with a cylindrical ceramic reactor. A schematic of the experimental apparatus is shown in Figure 1. Upon introduction of a test sample with 2 g weight, the tube furnace was heated from room temperature to 800°C at the rate of 30°C/min. The airflow was 2.5 dm^3/min . From the moment the temperature of 800°C was attained, the

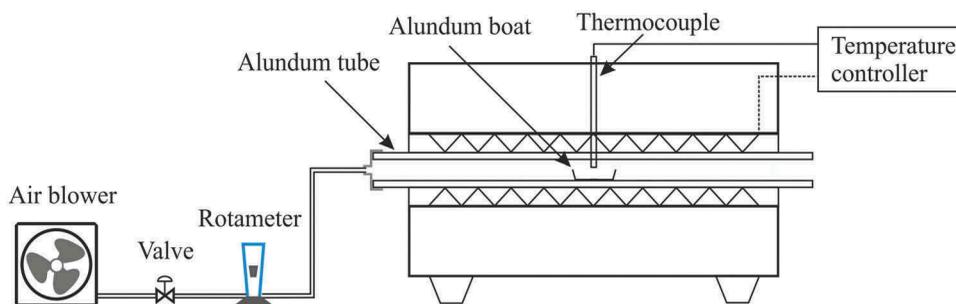


Figure 1. Schematic diagram of the tube furnace system.

Table 2. Coal and ash analysis.

Ultimate analysis (dry, %)						Proximate analysis (as received, %)						
C	H	N	S	Cl	O ^{diff}	M	A	VM	FC			
71.42	4.67	1.2	1.4	0.647	12.5	7.7	7.6	32.42	52.33			
Trace elements in coal (dry, mg/kg)												
As	B	Ba	Co	Cr	Cu	Li	Mo	Ni	Pb	Sr	V	Zn
1.6	125	89.4	4.51	13.9	10.2	17.8	1.41	10.1	33.3	32.4	19.5	63.3
Chemical composition of ash (wt %)												
SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Mn ₃ O ₄	TiO ₂	CaO	MgO	P ₂ O ₅	SO ₃	Na ₂ O	K ₂ O		
29.0	18.3	16.45	0.39	0.8	11.0	5.55	0.38	11.9	4.55	0.76		

sample was kept in the furnace for 20 min. After this time, the ash was immediately removed from the cylindrical reactor, cooled to room temperature, and then stored in a desiccator.

Bottom ash analysis

Each sample was analyzed twice. TEs in ash were determined using the ICP-OES method with the use of plasma spectrometer Thermo iCAP 6500 Duo ICP. The residue rate (R), which is the ratio of the TE concentration in ash ($C_{TE,ash}$) to the concentration of TE introduced to the combustion system ($C_{TE,in}$), has been utilized to describe the efficiency of retention TEs in ashes. The residue rate was calculated using the following equation (1):

$$R = \frac{C_{TE,ash} \cdot A}{C_{TE,in}} \cdot 100\% \quad (1)$$

where A represents the share of ash formed from combustion. For samples of coal and coal with 5% and 10% addition of HL, the A values were as follows: 0.82; 0.145; 0.180. The mentioned values were determined experimentally, after combustion the samples in the dry state.

Thermodynamic equilibrium calculations

The predicting of compound formation containing TEs was performed in FactSage 6.3 software. The thermodynamic equilibrium state of coal combustion and coal with HL additions was calculated in the 'Equilib' module for the following conditions: $T = 800^\circ\text{C}$, $p = .1 \text{ MPa}$ and $\lambda = 1.4$. Input data for the calculations comprised sets: coal, HL (presented subsequently in Tables 2 and 3) and combustion air. Thirty elements in total, which indicates the complexity of the calculations. The following thermodynamic databases were used: FToxid, FactPS, SGPS.

Results and discussion

Composition of coal and hydrated lime

Table 2 presents analyses of coal and chemical composition of ash. Based on ultimate and proximate analysis of coal and ash composition, the molar ratio of Ca/S has been established at $= 0.36$. Low value of Ca/S in coal indicates the need to use a flue gas desulphurization system. The tested coal can be classified as low-ash, as in the reference state (received basis), it contains 7.6% of ash. Moreover, 16 TEs have been identified in the coal, yet three of them were below the determination range of the equipment, i. e. Sn ($< 10 \text{ mg/kg}$), Ag ($< 0.7 \text{ mg/kg}$) and Rb ($< 1.0 \text{ mg/kg}$). B is the most abundant of the TEs in the tested coal, and concentrations of as many as 10 of them exceed 10 mg/kg .

The chemical composition of HL with division into main and minor compounds and TEs are presented in Table 3. Major components of HL are $\text{Ca}(\text{OH})_2$ and CaCO_3 , as shown by the XRD

Table 3. Normalized composition of HL based on various research methods.

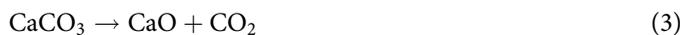
Analysis of dry hydrated lime – research methods	
<i>Mineralogical composition (%) – TG & XRD</i>	
Ca(OH) ₂	90.03
CaCO ₃	6.55
<i>Other minor chemical components (%) – WD-XRF</i>	
MgO	1.165
SiO ₂	0.91
SO ₃	0.446
Al ₂ O ₃	0.383
Fe ₂ O ₃	0.35
K ₂ O	0.064
MnO	0.040
Cl	0.019
<i>Trace elements (mg/kg) – ICP-OES</i>	
As	4.13
Ba	22.7
Cr	3.5
Cu	0.981
Li	6.45
Ni	3.98
Pb	3.19
Sr	265
V	7.23
Zn	30.7

analysis presented in Figure 2. Percentage contents of Ca(OH)₂ and CaCO₃ shown in Table 3, were calculated including mass stoichiometric reaction ratios (2) and (3) and weight losses within thermal decomposition of each mineral in TG tests realized in synthetic air atmosphere according to Figure 3. The HL composition was calculated to dry state, and having considered the XRF analysis it was normalized to 100%. Initial weight of HL sample in TG/DTG tests was 47 mg, and the heating rate was 10°C/min.

The DTG curve shown in Figure 3 demonstrates two ‘peaks’ of weight loss. The major weight loss is contained in temperature range approx. 350 ÷ 550°C and it is associated with Ca(OH)₂ dehydration reaction:



From 550 ÷ 950°C a lower weight loss occurs, which associates CaCO₃ decomposition according to the reaction occurring during calcination:



Based on mass spectrometry, gaseous H₂O and CO₂ ions released from HL sample were identified. Peaks on QMID curves in the function of temperature shown in Figure 3 confirm the course of reactions (2) and (3), and evaporation of moisture from lime, where temperature < 350°C.

Concentrations of 10 TEs are shown in Table 3, as the remaining elements (Cd, Co, Mo, Sn, Ag, Rb, B, and Zr) were present below the limit of determination of the equipment. Special attention should be paid to Sr, the concentration of which is 265 mg/kg HL, and it is as much as eight times higher than in the studied coal. In addition, in the case of As, a higher concentration in HL than in coal was found.

Coal and hydrated lime particle size distributions

Fuel particle size distribution strongly influences the efficiency of combustion, the amount of volatile ashes and pollution emission (Xue and Wang 2013). The particle sizes applied in the present study are smaller than 600 μm for coal, and 160 μm for HL. Coal particle sizes < 600 μm are applied in pulverized-coal boilers and in CFB boilers (Ramírez Behainne et al. 2009; Xue and Wang 2013).

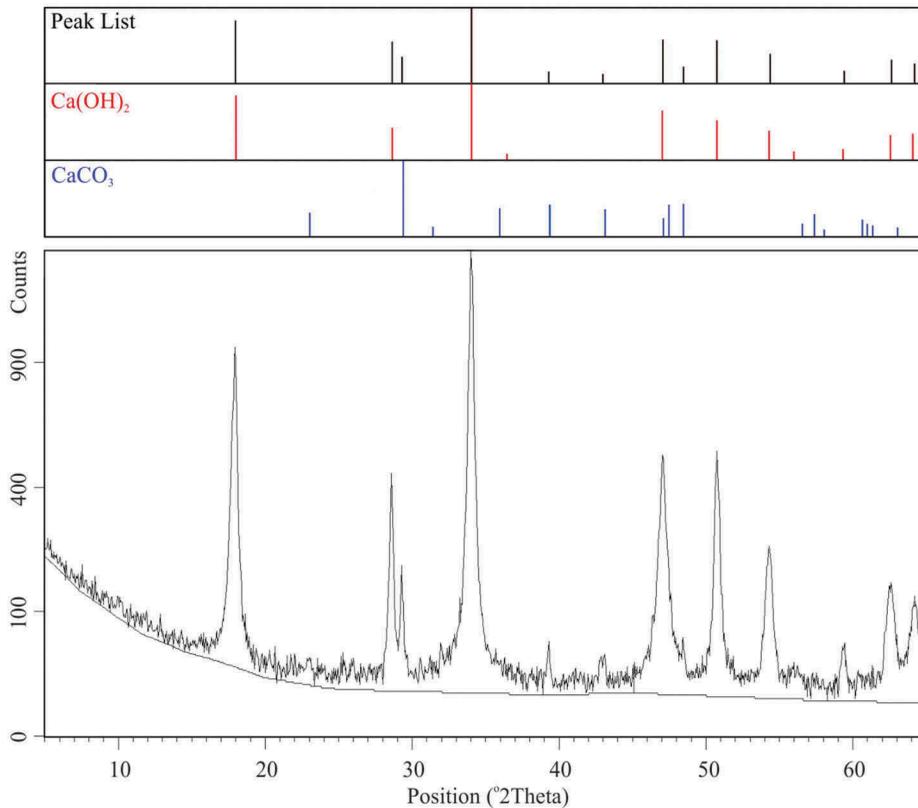


Figure 2.

Figure 4(a,b) compares distribution functions of particle size distributions (Q3) and percentage shares of particle sizes (p3) for coal and HL. Particle size distributions for coal and HL are unimodal, with peak falling on 262 μm for coal and 10 μm for HL. HL particle size distribution is close to symmetry, whereas for coal it is moderately symmetrical.

TEs in bottom ashes

The subject of the analyses are ash samples from coal combustion, 100% coal + 5% wt. HL and 100% coal + 10% wt. HL, for which molar ratios (Ca/S) are 0.36; 1.81; 3.26, respectively. Thirteen TEs were identified in samples of bottom ashes and each determination was performed twice. The influence of HL added to coal on the retention of TEs in bottom ashes was evaluated based on the residue rate (R) expressed with equation (1), and the results are shown in Figure 5(a–m). TEs present in bottom ashes were divided into three groups in terms of change of the value of R rate with addition of HL to coal.

The 1st group included: As, B, Co, Li, Mo, and V, for which R increases with HL addition, according to Figure 5(a–f). By interpreting the results of experimental tests in the range 0–10% wt. HL, the highest improvement of R (by approx. 12%) was obtained by Co and Mo, and lowest for B (by approx. 4%). The highest rate ($R > 80\%$) in 1st group is shown by As, Li and B. High R_{As} and R_{B} are particularly desirable in ash, as according to Nalbandian (2012) emission of those elements from coal combustion raises the greatest environmental concerns. An analysis of thermodynamic calculations, a clear impact of HL added to coal has been observed on the ash components

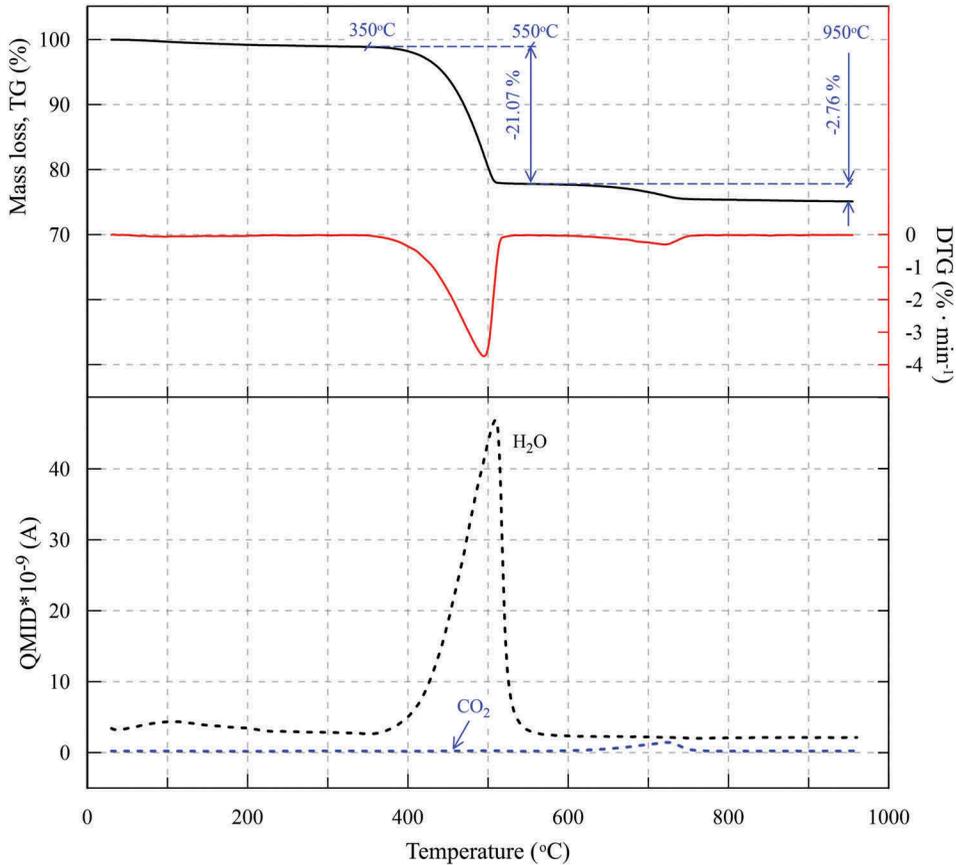
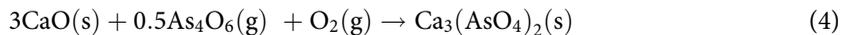


Figure 3. Thermal curves TG, DTG and QMID for HL.

containing TEs, which are mentioned in Table 4. Arsenic is present in the ash from coal combustion in the form of AlAsO_4 (s), and As_2O_3 (l) – in liquid slag phase (A-Slag). When 10 wt.% HL was added to coal, liquid slag phase was not formed, and As was found in the following ash components: $\text{Ba}_3(\text{AsO}_4)_2$ (s), $\text{Ca}_3(\text{AsO}_4)_2$ (s) and Li_3AsO_4 (s). Interestingly, based on the calculations the main compound responsible for retention of As in ash is $\text{Ba}_3(\text{AsO}_4)_2$ (s). No information on the possibility of $\text{Ba}_3(\text{AsO}_4)_2$ (s) formation has been provided in the literature thus far. As reported by Bartoňová and Klika (2014) and Junying et al. (2007), the addition of CaO to coal combustion enhances As retention in bottom ash as a result of the following reaction:



On the other hand, $\text{Ba}_3(\text{AsO}_4)_2$ (s) formation may stem from the following reaction:



The Gibbs energies (ΔG) for (4) and (5) reaction in 800°C calculated in the FactSage software are as follows: -482.3 kJ, -841.7 kJ. Reaction (5) has a higher priority than (4) due to considerably lower ΔG value.

The calculation results presented in Table 4 indicate that B and V in coal ash form compounds with Mg: $\text{Mg}_2\text{B}_2\text{O}_5$ (s), $\text{Mg}_3(\text{BO}_3)_2$ (s), $\text{Mg}_2\text{V}_2\text{O}_7$ (s), and addition of HL to coal favors B and V retention in the following salts: $\text{Ca}_3(\text{BO}_3)_2$ (s), $\text{Ca}_3(\text{VO}_4)_2$ (s). On the other hand, during coal

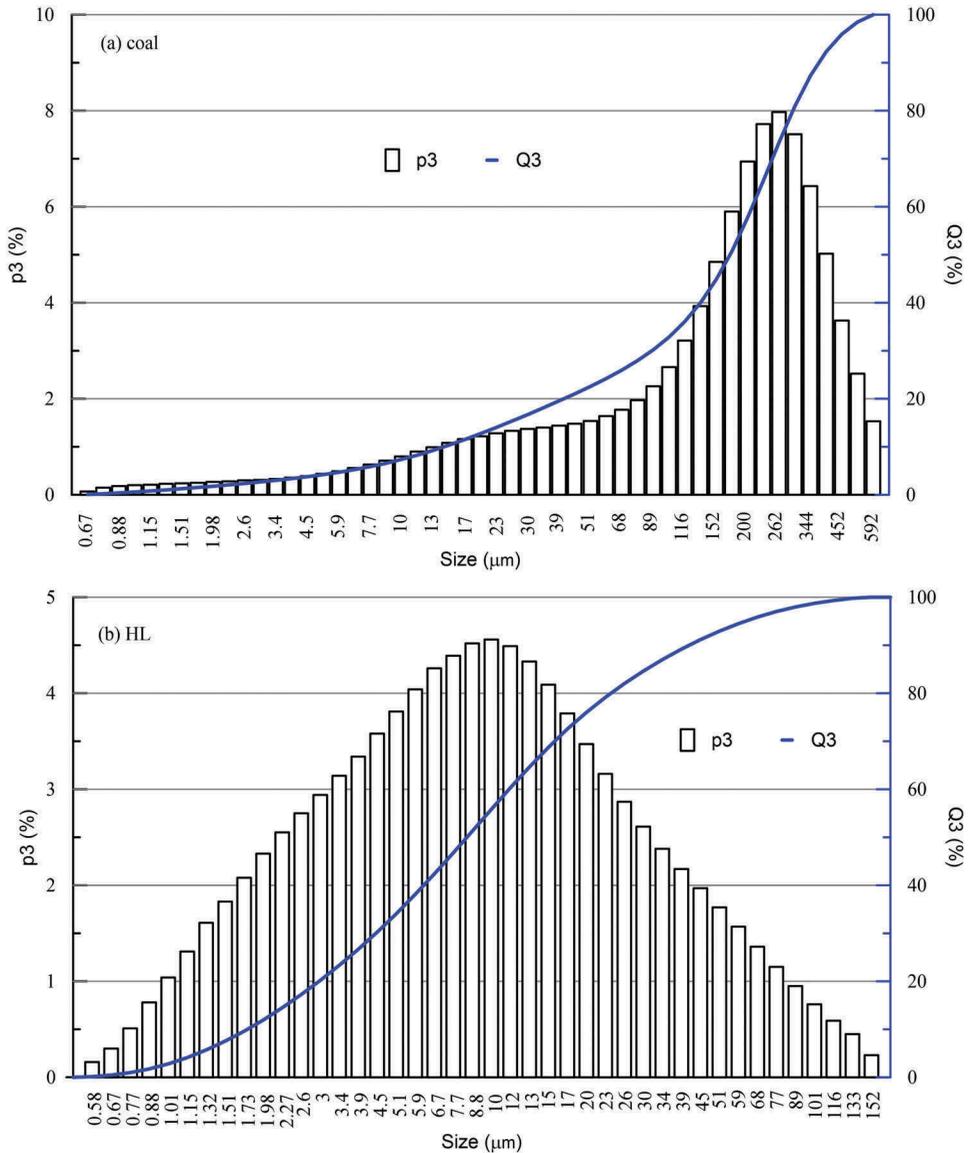


Figure 4. Particle size distribution and cumulative distribution for: (a) coal, (b) HL.

combustion the entire Mo is released to flue gases primarily as $\text{H}_2\text{MoO}_4(\text{g})$ and $\text{Mo}(\text{ClO})_2(\text{g})$. However, a 5% wt. HL addition to coal is enough to enable Mo retention in the form of $\text{CaMoO}_4(\text{s})$.

According to Figure 5(g-i), the 2nd group included Ba, Cr, and Zn. These elements do not exhibit a clear direction of changes for the R rate with HL addition to coal. Therefore, it has been determined that HL addition to coal does not have a significant impact on Ba, Cr and Zn retention in bottom ash. Addition of CaO does not improve Cr retention in coal, which has been confirmed by Cheng et al. (2001), among other authors. CaO addition to combustion chamber results in ash dilution, which may lead to reduced Cr and Zn retention degree (Bartoňová and Klika 2014). However, this does not alter the fact that the R obtained in the present study for Ba, Cr, and Zn in the coal bottom ash is high (> 65%), which is in line with the reports of Wu and Barton (2001), Duan et al. (2016). An interpretation of calculation results in the thermodynamic equilibrium state

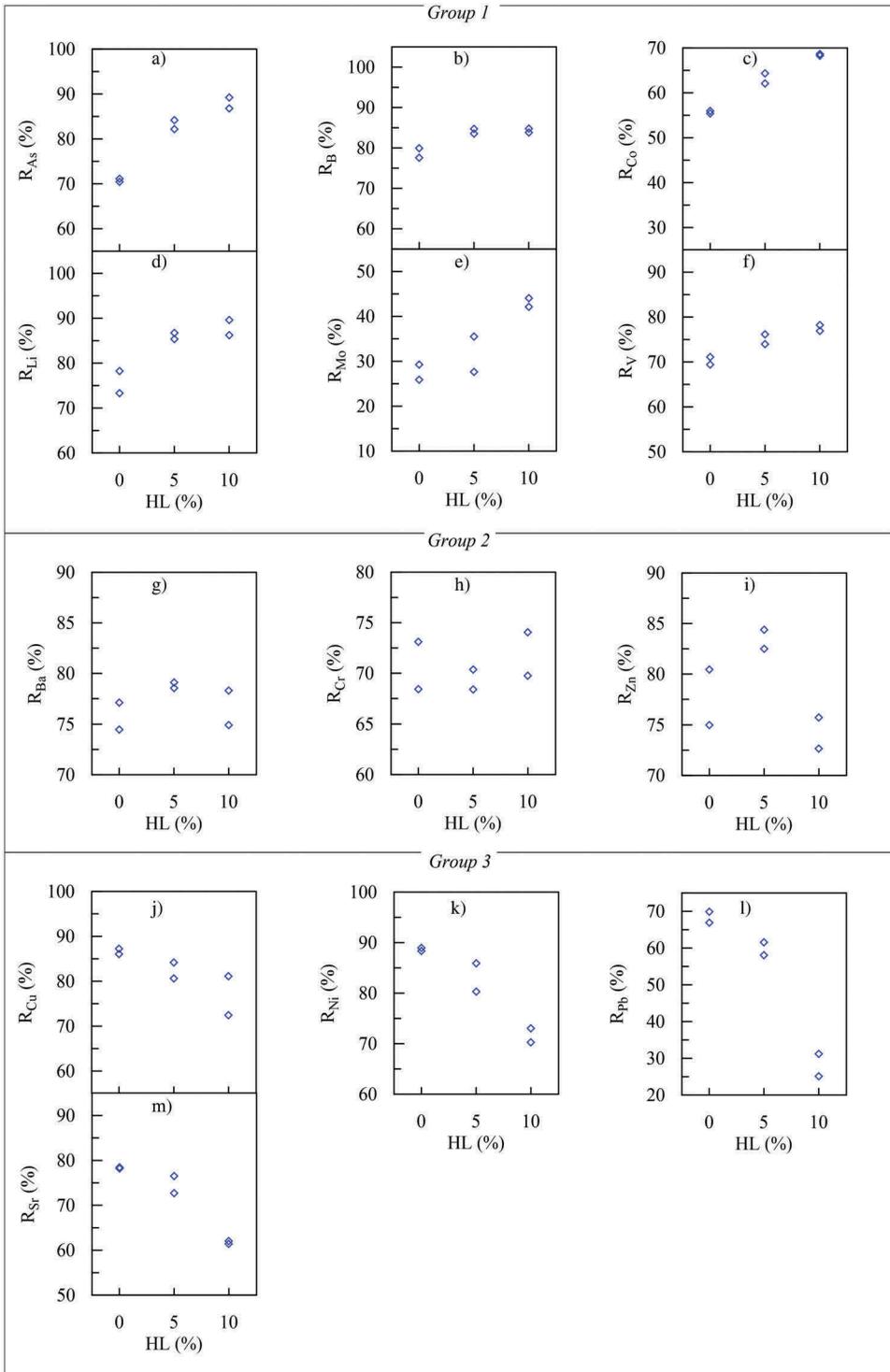


Figure 5. Influence of HL addition to coal on residue rates TEs in bottom ashes.

Table 4. The effect of adding HL to the coal combustion on species containing TEs in ash at 800°C.

HL (%)	0	0 and 5	5 and 10
Ash phase	solid	liquid slag	solid
As	AlAsO ₄	As ₂ O ₃	Ba ₃ (AsO ₄) ₂ , Ca ₃ (AsO ₄) ₂ , Li ₃ AsO ₄
B	Mg ₂ B ₂ O ₅ , Mg ₃ (BO ₃) ₂		Ca ₃ (BO ₃) ₂
Ba	BaSO ₄		BaCrO ₄ , BaSO ₄ , Ba ₃ (AsO ₄) ₂
Co	CoFe ₂ O ₄	CoO	CoO
Cr	Cr ₂ O ₃		Cr ₂ O ₃ , BaCrO ₄
Cu		Cu ₂ O	
Li	Li ₂ SO ₄		Li ₃ AsO ₄
Mo			CaMoO ₄
Ni	NiTiO ₃	NiO	NiO, NiFe ₂ O ₄
Pb		PbO	
Sr	SrSO ₄		SrTiO ₃ , SrMn ₃ O ₆
V	Mg ₂ V ₂ O ₇		Ca ₃ (VO ₄) ₂
Zn	ZnAl ₂ O ₄	ZnO	ZnO, ZnAl ₂ O ₄

allowed noticing that HL addition to coal reduces weight contribution of BaSO₄(s) and ZnO(l) in ash and promotes BaCrO₄(s), Ba₃(AsO₄)₂(s) and ZnO(s) formation. As demonstrated in Table 4, none of the elements classified in the 2nd group forms compounds with Ca in ashes.

Cu, Ni, Pb and Sr belong to the last, 3rd group distinguished in Figure 5(j–m), for which the increase in HL content in combustion chamber means a decrease of R. As much as 70% Pb was retained in the bottom ash from coal, which may stem from: the used combustion method, low combustion temperature of 800°C, and favorable composition of ash – rich in SiO₂, which belongs to the major compounds favoring Pb retention (Zhou et al. 2018). The possibility of retention of as much as 80% Pb in ash have been confirmed by the experiments of Tang et al. (2017), who used tube furnace at temperature 800°C to burn municipal solid waste.

Among all TEs analyzed in this study, the highest R values in ash from coal were obtained for Cu and Ni (> 80%). When 10% HL was added to coal, the highest reduction-characterized R_{Pb} (approx. 40%). The R_{Cu}, R_{Ni}, R_{Pb} reduction during HL addition may stem from disappearance of liquid slag phase, as it is suggested by the calculation results provided in Table 4. Cu and Pb in ashes from coal and coal with 5% HL is located solely in the liquid slag phase as Cu₂O(l) and PbO(l). The disappearance of liquid phases is accompanied by Cu and Pb release to flue gases, primarily to CuCl(g) and PbCl₂(g).

On the other hand, the cause for the unfavorable decrease of R_{Sr} following the addition of HL to coal may be seen in the high Sr content in HL of 265 mg/kg. Sr added from HL, based on equilibrium calculations is released primarily as KSrCl₃(g).

Conclusions

The subject of the present study was to verify the impact of industrial HL addition to coal on the retention of TEs in bottom ashes. Analysis of the residue rates of the 13 TEs identified in the ashes has been performed by dividing the elements into three groups. The most favorable effect of HL addition to coal on TEs retention in ash was found for As, B, Co, Li, Mo, and V – these elements were classified in the 1st group. Lack of a clear change tendency for the residues with the addition of calcium was revealed for Ba, Cr and Zn – assigned to the 2nd TEs group. On the other hand in the case of TEs of the 3rd group, a negative impact of the added calcium was found for Cu, Ni, Pb and Sr retention in the ash.

Interpretation of the thermodynamic modeling results confirmed that As, B, Mo, and V – that is TEs of the first group, react with HL added to coal creating the respective compounds: Ca₃(AsO₄)₂(s), Ca₃(BO₃)₂(s), CaMoO₄(s) and Ca₃(VO₄)₂(s). Moreover, the addition of HL to coal reduces the formation of liquid slag phase containing, among others, TEs in the following form: As₂O₃(l), CoO(l), Cu₂O(l), NiO(l), PbO(l), and ZnO(l). Compounds present in the ash, such as Ba₃(AsO₄)₂(s),

$\text{Li}_3\text{AsO}_4(\text{s})$, and $\text{BaCrO}_4(\text{s})$ constitute a proof of the significance of inclusion of the highest possible number of TEs contained in the fuel in calculations.

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