

# Effect of CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in coal ash on the retention of acid-forming elements during coal combustion

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*Abstract:* - Industrial coal combustion ashes as well as laboratory-scale experiments were used for the evaluation whether CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> can help with the retention of volatile and acid-forming elements (S, Cl, Br, As and Se). Both industrial ashes evaluation and laboratory combustion experiments lead to the conclusion that CaO can efficiently help with the capture of not only S, but also of Cl, Br, As and Se.

*Key-Words:* Coal combustion, desulphurization, limestone, trace elements, emissions, sulphur, chlorine, bromine, arsenic, selenium

## 1 Introduction

Fluidised-bed combustion and gasification represents modern and efficient way how to reduce emissions of many pollutants [1-3]. Owing to low combustion temperature, formation of nitrogen oxides is significantly reduced, possibility of co-combustion of coal and biomass can help to decrease amount of toxic elements in emissions and solid combustion products [4], desulphurization additives can significantly reduce amount of sulphur oxides in emissions [5-7] etc. However, even if modern combustion technology is used, it is still accompanied by the release of toxic pollutants into surrounding atmosphere [8-13].

In contrast to coal pyrolysis where heavy metals tend to remain in solid products [14], during coal combustion most elements are (to greater or lesser extent) present in flue gas, which can easily come through the particulate control device. For this reason, great attention has been paid to possible condensation / adsorption of toxic elements on carbonaceous particles in fly ash [15-19]. Simultaneously, possible interactions of toxic volatile elements with Ca-based compounds are being studied intensively as well [7,9,20,21].

There are two main approaches for the evaluation of possible interactions of studied elements and Ca-bearing minerals – either performing laboratory-scale experiments or evaluation of industrial-scale coal-combustion ashes. Both approaches have their advantages and drawbacks.

Major advantage of evaluation of power-station coal combustion ashes is that they have been

created under real industrial conditions. The main drawback of this approach is that such experiments are very expensive and for this reason, only a couple of combustion tests can be performed. Furthermore, if more major components have similar distribution within the particle-size fractions, it could sometimes be rather problematic for mathematic evaluation to distinguish unambiguously between these factors, i.e., which one is the most important and which ones only have similar distribution.

In contrast to industrial-scale ashes evaluation, during laboratory tests, studied parameter can be changed while the other ones remain at the same level. However, the main drawback is the exact simulation of the real power station conditions, because the combustion temperature is not the only important parameter affecting elemental behaviour.

## 2 Problem Formulation

For the reasons mentioned above, in this work, the effect of CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> on the retention of S, Cl, Br, As and Se was studied using industrial-scale ashes and the results obtained were verified by laboratory-scale combustion tests with the same coal and the same limestone to avoid misleading conclusions.

## 3 Problem Solution

### 3.1 Combustion unit, samples, methods

### Power-station combustion

For this study, samples of coal, limestone, bottom ash and cyclone ash were collected during atmospheric circulating fluidised-bed combustion at thermal power station. The bituminous coal was combusted there with limestone due to desulphurization of emissions at the combustion temperature of about 850°C.

Collected samples were ground, homogenized and analysed for the elemental content by means of polarized-beam X-ray spectrometry on SPECTRO XEPOS. Particle-size fractions of bottom ash and cyclone ash were prepared on sieves. Ash content was determined gravimetrically in muffle furnace at 815°C.

### Laboratory-scale combustion

Laboratory combustion experiments were performed in muffle furnace where the same bituminous coal and the same limestone were combusted in a mixture. The combustion temperature was selected to be the same as during coal combustion in fluidised-bed power stations [12] – i.e. 850°C.

The weight percentage of limestone in the combustion blend was 0% (test 1), 1.3% (test 2), 3.7% (test 3), 5.9% (test 4), 10.0% (test 5), 11.1% (test 6) and 13.0% (test 7). All combustion tests were performed in duplicate and average volatility of each studied element (S, Cl, Br, Se, As) was calculated.

Analyses of input materials (coal and limestone) and of ashes created during the combustion were performed by means of X-ray fluorescence spectrometry on SPECTRO XEPOS.

## 3.2. Results and discussion

### 3.2.1 Industrial coal combustion

Ash contents and the results of chemical analysis of the coal, limestone, bottom ash and cyclone ash collected at fluidised-bed thermal power station are summarized in Table 1. Elemental composition of particle-size fractions of the bottom ash and the cyclone ash is given in Table 2 and Table 3.

Results of the chemical analyses of studied ashes were used for the evaluation of mutual relations of acid-forming elements (S, Cl, Br, As and Se) and CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> contents. Calciumoxide represents the product of thermal decomposition of limestone added to the coal during the combustion. Al<sub>2</sub>O<sub>3</sub> documents the effect of the clay minerals (that were abundant in the parent coal) and Fe<sub>2</sub>O<sub>3</sub> was originally present there as Fe-

sulphides / disulphides and due to rather high content in ashes its effect was evaluated as well. SiO<sub>2</sub> was not selected for the evaluation because adsorption of elements onto aluminosilicates are better documented by Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub> bound in the form of quartz usually adsorb significantly lesser amount of elements than other clay minerals occurring in coals – e.g. kaolinite, illite or mica).

To avoid misleading conclusions, mutual relations of CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> should also be taken into account. For this purpose, correlation coefficients between CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are given in Table 4 (for bottom ash fractions) and in Table 5 (for cyclone ash fractions). The data summarized in Tables 4 and 5 suggest that distribution of these elements within the particle-size fractions of both the bottom ash and the cyclone ash is absolutely different.

Table 1 Ash content and elemental composition of coal (C), limestone (L), bottom ash (BA) and cyclone ash (CA) collected at thermal power station.

	C	L	BA	CA
Ash (%)	19.13	57.45	94.07	97.01
MgO (%)	0.67	0.47	1.41	2.78
Al <sub>2</sub> O <sub>3</sub> (%)	3.25	0.21	24.11	10.18
SiO <sub>2</sub> (%)	8.10	1.78	57.42	29.18
P <sub>2</sub> O <sub>5</sub> (%)	0.09	0.31	0.11	0.29
K <sub>2</sub> O (%)	0.43	0.001	3.45	1.26
CaO (%)	1.15	52.64	2.21	37.12
MnO (%)	0.02	0.007	0.05	0.122
Fe <sub>2</sub> O <sub>3</sub> (%)	1.25	0.33	4.39	6.89
S (%)	1.02	0.08	0.17	2.95
Cl (ppm)	3080	406.8	807	9183
As (ppm)	11.0	1.0	2.3	2.7
Se (ppm)	1.3	3.3	0.8	1.2
Br (ppm)	26.0	1.0	5.3	49

Table 2 Ash content and elemental composition of particle-size fractions of the bottom ash

	Particle-size fractions (mm)						
	< 0.09	0.09 – 0.2	0.2 – 0.4	0.4 – 0.6	0.6 – 1.0	1.0 – 2.0	> 2.0
Ash (%)	81.2	97.55	98.57	98.34	97.25	90.09	94.2
MgO (%)	1.94	1.85	1.84	1.31	1.48	1.56	1.16
Al <sub>2</sub> O <sub>3</sub> (%)	18.31	15.33	20.63	19.89	20.53	20.93	25.05
SiO <sub>2</sub> (%)	41.41	51.37	57.73	59.43	59	54.98	58.98
P <sub>2</sub> O <sub>5</sub> (%)	0.18	0.16	0.15	0.12	0.1	0.11	0.1
K <sub>2</sub> O (%)	1.2	1.32	2.64	3.36	3.61	3.49	3.82
CaO (%)	13.32	13.53	7.48	4.94	2.67	1.67	0.57
MnO (%)	0.03	0.04	0.05	0.05	0.06	0.06	0.04
Fe <sub>2</sub> O <sub>3</sub> (%)	3.83	3.93	3.96	4.23	4.90	4.93	4.21
S (%)	1.10	1.02	0.22	0.13	0.17	0.28	0.09
Cl (ppm)	4650	4440	2930	1557	1051	568	225
As (ppm)	1.7	1.8	1.8	2.0	3.0	1.7	2.1
Se (ppm)	1.3	1.3	1.2	1.0	1.1	1.0	0.8
Br (ppm)	18	16	13	11	8	6	3

Table 4 Mutual correlation coefficients between contents of major element oxides in the bottom ash

	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
CaO	1	-0.847	-0.742
Al <sub>2</sub> O <sub>3</sub>		1	0.346
Fe <sub>2</sub> O <sub>3</sub>			1

Table 5 Mutual correlation coefficients between contents of major element oxides in the cyclone ash

	CaO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>
CaO	1	-0.908	0.226
Al <sub>2</sub> O <sub>3</sub>		1	-0.388
Fe <sub>2</sub> O <sub>3</sub>			1

Data shown in Tables 2 and 3 were used for the calculation of the mutual (pair) correlation coefficients between 5 acid-forming elements (S, Cl, As, Se and Br) and CaO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> for both the bottom ash and the cyclone ash fractions.

Calculated values obtained for S, Cl, As, Se and Br are given in Figs. 1-5 (each studied element has its own figure where correlation coefficients with Al<sub>2</sub>O<sub>3</sub>, CaO and Fe<sub>2</sub>O<sub>3</sub> contents in the bottom ash and cyclone ash fractions are plotted).

All five volatile acid-forming elements (S, Cl, Br, As and Se) show rather similar behaviour – the highest correlation coefficients were calculated for their relations with CaO contents. Effect of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in the studied ashes was generally of minor or negligible significance.

Table 3 Ash content and elemental composition of particle-size fractions of the cyclone ash

	Particle-size fractions (mm)						
	< 0.04	0.04-0.063	0.063-0.08	0.08-0.09	0.09-0.20	0.20-0.4	>0.4
Ash (%)	88.12	92.87	97.54	98.6	98.58	98.82	90.85
MgO (%)	1.56	2.44	2.94	3.61	2.62	1.51	1.35
Al <sub>2</sub> O <sub>3</sub> (%)	3.49	6.21	10.36	10.29	10.49	19.54	24.59
SiO <sub>2</sub> (%)	3.72	11.44	22.99	27	40.66	49.15	41.87
P <sub>2</sub> O <sub>5</sub> (%)	0.25	0.32	0.33	0.35	0.26	0.16	0.15
K <sub>2</sub> O (%)	0.29	0.66	1.2	1.11	1.49	1.79	1.95
CaO (%)	66.67	51.72	37.71	36.31	26.94	16.52	14.76
MnO (%)	0.12	0.15	0.17	0.19	0.09	0.07	0.06
Fe <sub>2</sub> O <sub>3</sub> (%)	4.48	8.06	8.99	10.53	5.35	4.44	4.33
S (%)	5.4	5.07	4.02	3.61	1.44	0.31	0.32
Cl (ppm)	15714	14617	9850	9149	5551	2407	2222
As (ppm)	2.8	2.6	2.8	2.7	2.6	2.5	2.4
Se (ppm)	1.6	1.3	1.5	1.4	0.8	1	1.1
Br (ppm)	145	99	51	43	28	14	10

Fig. 1 Correlation coefficients for S in fluidised-bed power station ashes

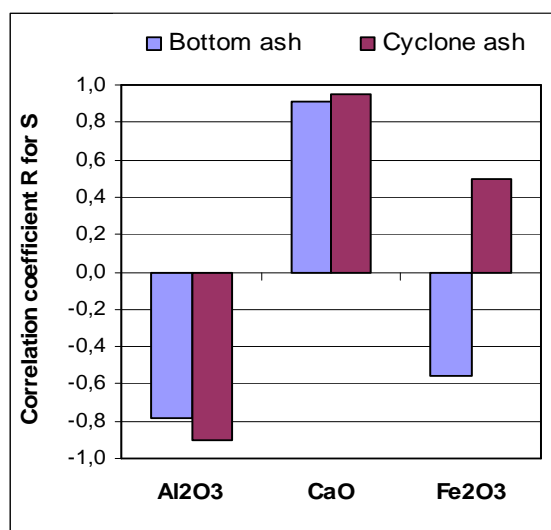


Fig. 2 Correlation coefficients for Cl in fluidised-bed power station ashes

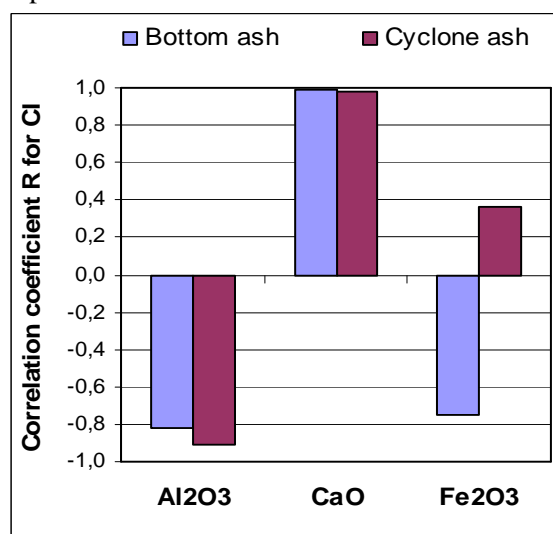


Fig. 3 Correlation coefficients for As in fluidised-bed power station ashes

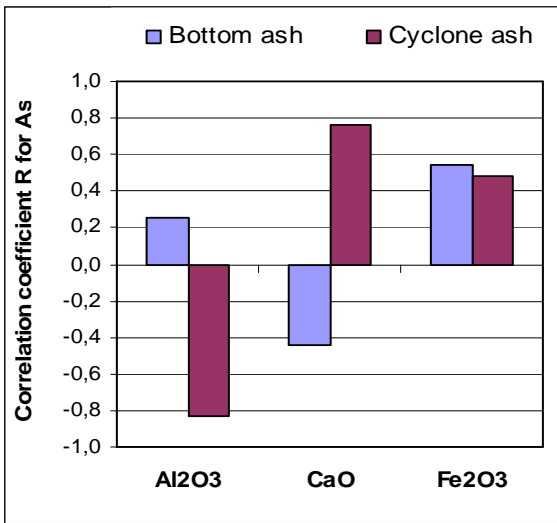


Fig. 4 Correlation coefficients for Se in fluidised-bed power station ashes

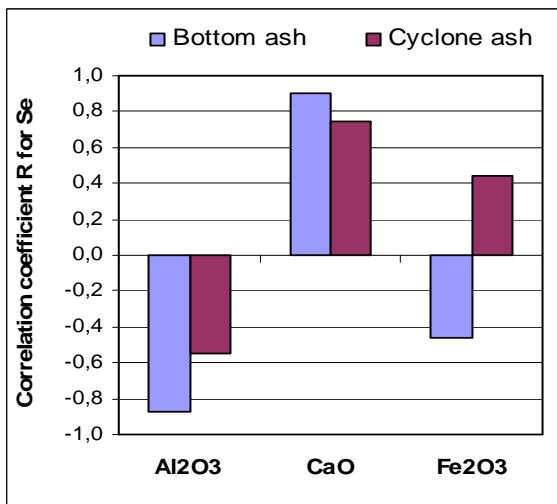
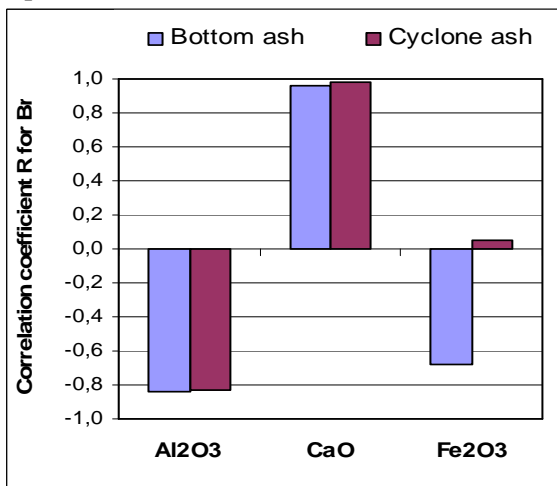


Fig. 5 Correlation coefficients for Br in fluidised-bed power station ashes



The only exception is the behaviour of As whose correlation coefficient with CaO in the bottom ash is negative while that with Fe<sub>2</sub>O<sub>3</sub> is positive. In cyclone ash, As exhibits the same behaviour as the other elements – it shows the highest correlation coefficient with CaO. Such behaviour can be explained through occurrence of As in pyrite (or other Fe- sulphides / disulphides), which is common mode of occurrence of As in coal. In bottom ash, some As is still associated with Fe, whereas in cyclone ash, longer time period available for the total pyrite decomposition brought about the release of As for the interaction with CaO.

Individual relations of S, Cl, As, Se and Br with CaO content in cyclone ash particle-size fractions are documented in Figs. 6-10.

Fig. 6 Mutual relation of S and CaO in cyclone ash

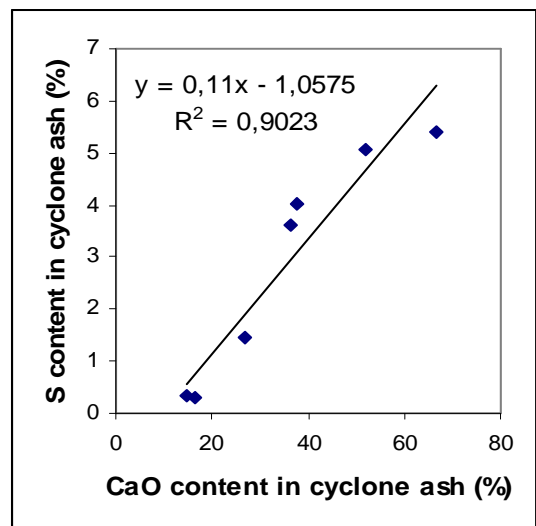


Fig. 7 Mutual relation of Cl and CaO in cyclone ash

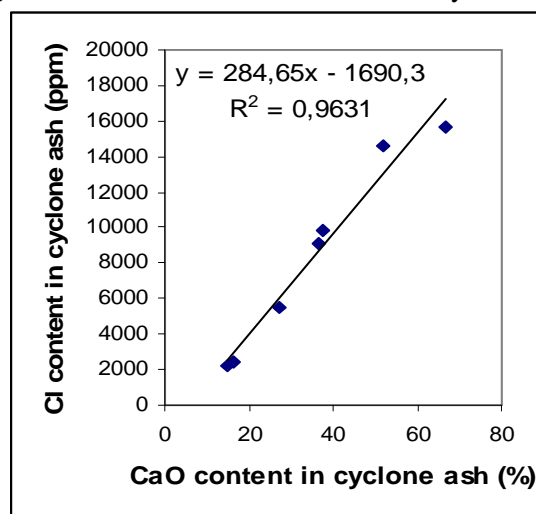


Fig. 8 Mutual relation of As and CaO in cyclone ash

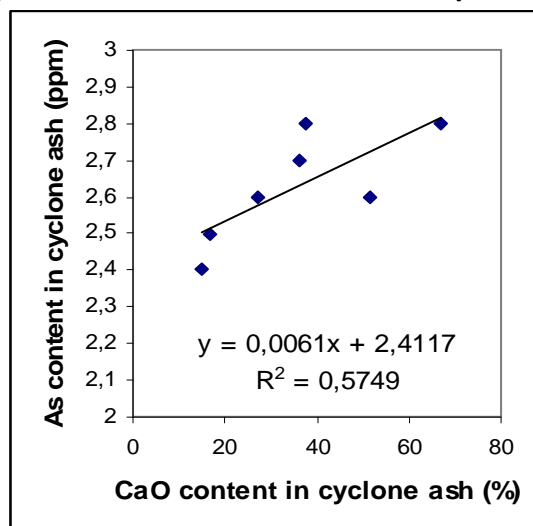


Fig. 9 Mutual relation of Se and CaO in cyclone ash

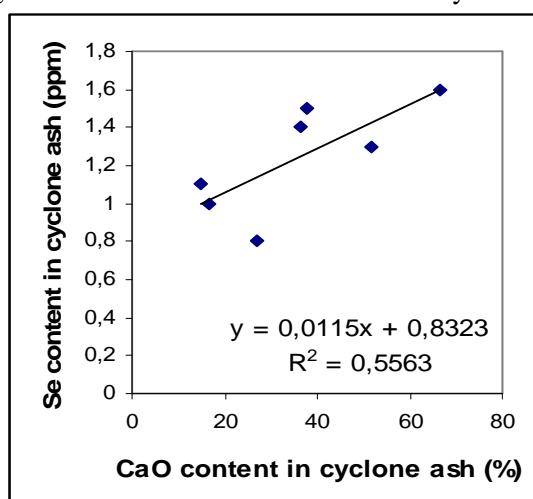
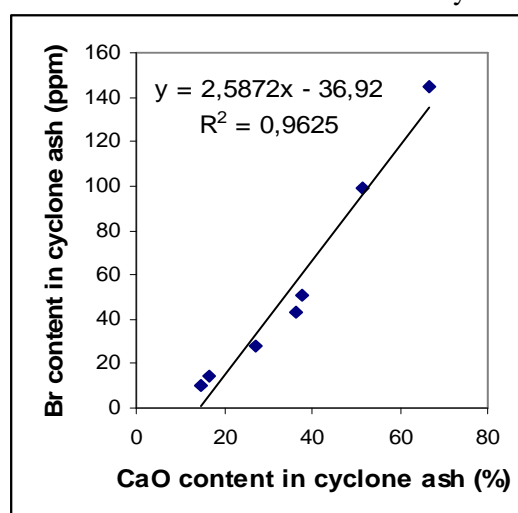


Fig.10 Mutual relation of Br and CaO in cyclone ash



In other words, the data obtained from industrial coal combustion in the power station indicate that it was CaO that has the most important effect on the behaviour of S, Cl, Br, As and Se.

Since the effect of CaO content (available for the interactions with the studied elements) can easily be simulated by different percentage of limestone blended with the coal, laboratory-scale experiments were conducted for this purpose. For the verification of the conclusion described above, laboratory combustion tests with the same coal, the same limestone and the same combustion temperature has been performed in muffle furnace.

### 3.2.2 Laboratory coal combustion

Behaviour of elements during laboratory-scale coal combustion was evaluated through the calculation of elemental volatility.

Volatility of elements (i.e., the percentage of given element that was released out of combusted blend of the coal and the limestone) was calculated according to Eq. (1):

$$V(\%) = 100 \cdot \left( 1 - \frac{m_{i,Ash}}{m_{i,CL}} \right) \quad (1)$$

$m_{i,CL}$  is mass of the i-th element in input combusted blend of coal and limestone (in g) and  $m_{i,Ash}$  is mass of the same i-th element in ash after the combustion (in g).

Mass of the i-th element in the ash ( $m_{i,Ash}$ ) was calculated according to Eq. (3):

$$m_{i,Ash} = 0.01 \cdot m_{Ash} \cdot w_{i,Ash} \quad (3)$$

where  $m_{Ash}$  is mass of the ash created during the combustion (in g) and  $w_{i,Ash}$  is mass fractions of the i-th element in this ash (in %).

Mass of i-th element contained in combusted blend of coal and limestone ( $m_{i,CL}$ ) was calculated using Eq.(2):

$$m_{i,CL} = 0.01 \cdot (m_L \cdot w_{i,L} + m_C \cdot w_{i,C}) \quad (2)$$

where  $m_L$  and  $m_C$  are masses of the coal and the limestone used for the combustion test (in g) and  $w_{i,C}$  and  $w_{i,L}$  are mass fractions of the i-th element in the coal and the limestone (in %).

Volatilities of S, As, Se, Cl, Br were calculated for all seven combustion tests (with increasing limestone content in the combusted blend) and the

averages of two duplicate measurements are given in Table 6.

Table 6 Average volatilities of S, Cl, Br, As, Se and Br during laboratory-scale combustion with increasing percentage of the limestone in the combusted blend with the coal

	Limestone	Volatility (%)				
		S	Cl	As	Se	Br
Test 1	0%	74	89	74	82	92
Test 2	1.3%	64	86	70	72	90
Test 3	3.7%	56	77	64	65	85
Test 4	5.9%	53	78	64	66	83
Test 5	10.0%	34	66	58	63	81
Test 6	11.1%	29	50	51	55	75
Test 7	13.0%	14	41	42	59	73

Decrease in volatility of S, Cl, Br, As and Se with the increasing amount of limestone in the combustion blend is for easier interpretation illustrated also in Fig. 11. Values given in Table 6 and plotted in Fig. 11 suggest that if no limestone was added, the volatility of all these 5 elements are very high (about 74-92 % of the combusted amount of these elements were volatilized). With gradual increase of limestone amount contained in the combusted blend, the linear decrease in the volatility has been observed for all these 5 acid-forming elements. Due to alkaline character of CaO, it can react with these 5 studied elements (with acid-forming properties). Probable chemical reactions are:

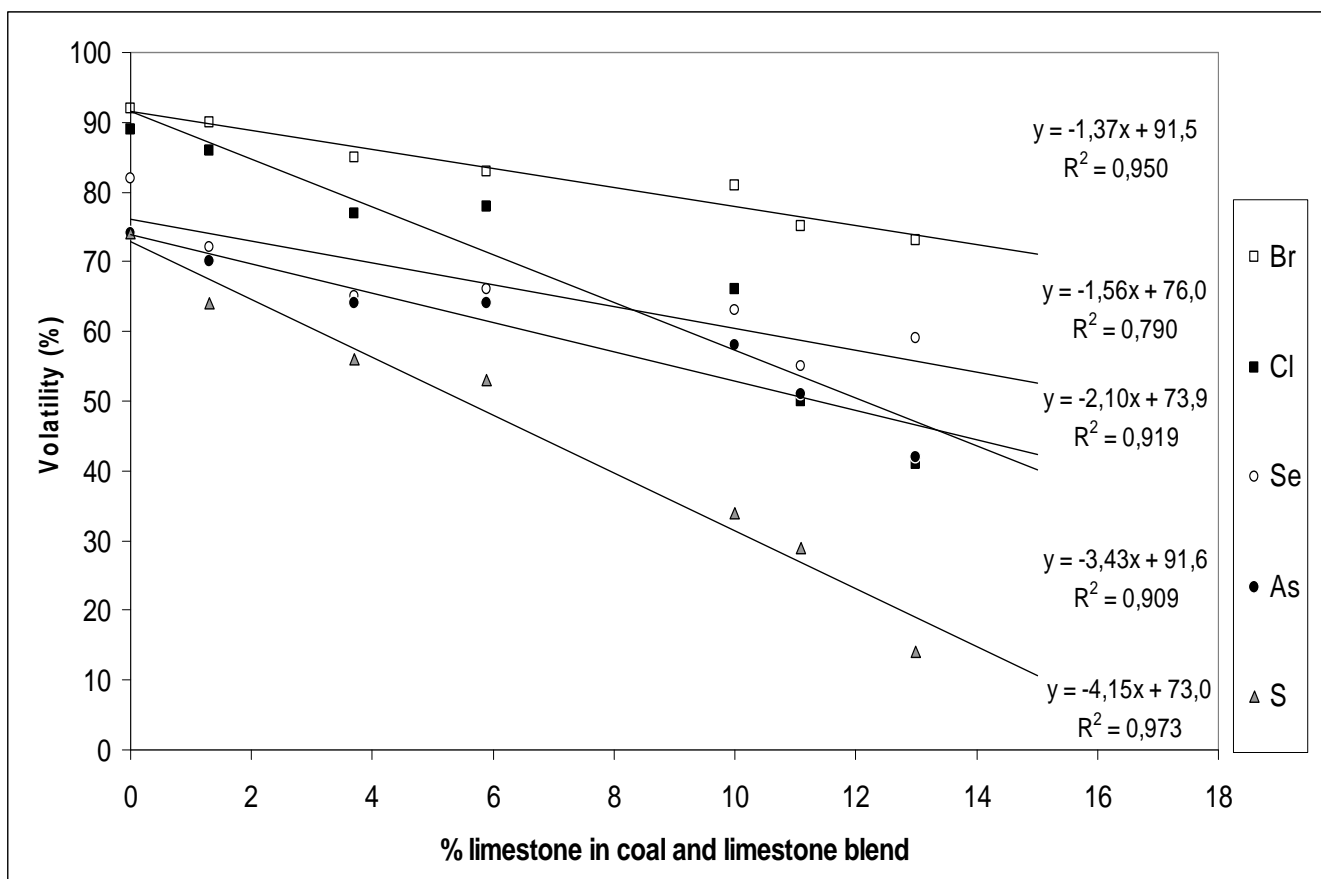
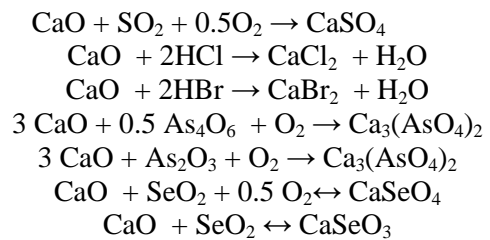


Fig. 11 Decrease in elemental volatilities with increasing amount of limestone in combusted blend with coal (results of laboratory combustion tests in the muffle furnace)

## 4 Conclusion

This work was conducted to evaluate effect of major element contents (CaO, Al<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>) on the behaviour of five volatile and acid-forming elements – S, Cl, Br, As, Se during coal combustion.

In the industrial coal combustion ashes, highest correlation coefficients were obtained for the relations of these elements with CaO. This conclusion was further verified by series of laboratory combustion tests where increasing amount of the limestone added to the same coal decreases gradually the volatility of these elements (S, Cl, Be, As and Se).

Thus, both industrial and laboratory-scale study lead to the conclusion that limestone added to coal during the combustion can help not only with the retention of S, but also with the capture of Cl, Br, As and Se.

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