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LETTER

Effect of CaO and Fe₂O₃ on Partitioning of As and S within Ash Fractions from Fluidised-Bed Co-Combustion of Coal and Wastes

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Abstract: Possible interaction of volatilized As and S with CaO and Fe₂O₃ (creating solid product) could efficiently improve coal combustion flue gas cleaning. For this reason, S-CaO, As-CaO, S-Fe₂O₃ and As-Fe₂O₃ relationships were evaluated in bottom ash and fly ash fractions from fluidised-bed co-combustion of coal and wastes (and limestone as desulphurization additive) through calculation of correlation coefficients and composition of magnetic concentrates. It was concluded that S exhibited a dominant association with CaO while As exhibited affinity to both CaO and Fe₂O₃ - the significance differed a little in bottom ash and fly ash. In the bottom ash, the affinity of As to CaO was more significant, while in the fly ash the association to Fe₂O₃ slightly prevailed.

Keywords: Coal combustion, Sulphur, Arsenic, CaO, Fe₂O₃, Flue gas cleaning, Retention.

1. INTRODUCTION

Fluidised bed combustion provides numerous advantages in comparison with predominant combustion systems, such as high combustion efficiency, reduced coal crushing, ability to use low-grade coals and alternative fuels (wastes, biomass, sewage sludge) [1, 2], *etc.* One of the most important advantages is low combustion temperature (below ash fusion temperature) facilitating easier ash removal and significantly reducing air pollution. Moreover, due to ground limestone/dolomite / CaO added during the combustion, the efficient desulphurization of emissions could be achieved.

The total amount of emissions from coal combustion power station is a complex phenomenon and depends on both operating conditions and the characteristics of the coal (*e.g.* trace elements in the coal) [3, 4]. Despite the progress in flue-gas cleaning technologies, fluidised bed combustion is still accompanied by emissions of numerous pollutants, such as heavy metals, toxic trace elements, or organic compounds *etc.* [5, 6]. As the retention efficiency of fabric filters and electrostatic precipitators is relatively high, the capture of gaseous fractions of volatile elements, such as Hg, As, Cl, Br, *etc* [7, 8] is more problematic (volatilized elements in gaseous form can easily pass through the particulate control device).

To solve this problem, there is an effort to capture the volatile elements from flue gas onto solid adsorbent. Activated carbon is one of the most effective adsorbents for the retention of Hg [9, 10] and it was tested for the retention of As and Se [11] as well. However, to reduce the cost, cheaper alternatives are also being sought. Unburned carbon (in fly ash) is one of the most promising alternatives [12 - 14] and was studied in terms of possible flue gas cleaning from Hg [15 - 17] and some other trace elements [18 - 21]. The major advantage of unburned carbon is its porosity and higher specific surface area [18, 22] in comparison with other ash grains; in combination with some functional groups it improves the retention of inorganic species [15 - 17] from flue gas or can be used for the retention of dyes from aqueous solutions [23]. In addition to carbonaceous materials, the retention of volatile elements was tested on kaolinite [24], MnO_x [25, 26] or desulphurization additives / calcareous adsorbents [27 - 29]. It is worth mentioning

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in this context that the percentage of CaO in fluidised-bed ashes is typically higher than that of unburned carbon (in some fractions it can reach even 50%) [29].

Desulphurization additives (lime, limestone *etc.*) are currently used for the retention of S. Except S, promising results on the possible retention of As on Ca-bearing compounds were reported as well [11, 29, 30]. However, some recent studies concluded that not only Ca but also Fe could provide sites for As association [11, 31 - 33]. The conclusion that As can be captured from flue gas on active sites of both Ca and Fe was based on thermodynamic equilibrium calculations [32] and laboratory-scale combustion [11, 31, 33]. Since As retention is a complex phenomenon, the results from real power stations are needed. Besides, fluidised-bed coal combustion ashes are advantageous for this study due to naturally high levels of Ca-bearing minerals (desulphurization additives) that can affect Fe₂O₃ interaction.

Possible association of volatilized As and S with CaO and Fe₂O₃ (creating solid product) could efficiently improve coal combustion flue gas cleaning. For this reason, herein, the relationships between S and As with CaO and Fe₂O₃ were evaluated in bottom ash and fly ash fractions from fluidised-bed co-combustion of coal and wastes (and limestone as desulphurization additive) through calculation of correlation coefficients and composition of magnetic concentrates.

2. METHODS

The samples of Bottom Ash (BA) and Fly Ash (FA) were collected at atmospheric circulating fluidisedbed power station where lignite was co-combusted with wood, bark, sewage sludge and solid recovered fuel (blend of shredded paper, plastics, wood, textiles, carpets *etc.*). Desulphurization of emissions was achieved by adding limestone as (dry) desulphurization additive. Fluidised-bed combustion typically does not require powdered coal (combustion efficiency is achieved by circulating in fluidised-bed and longer dwell time); therefore, only limestone was finely ground for efficient interaction with S in flue gas. Efficient combustion can be documented by low unburned carbon content in both BA (< 3%) and FA (< 1%).

During the whole combustion test, fractional samples of bottom ash and fly ash were collected at regular time intervals and mixed properly. From these composite samples, representative subsamples were separated by quartering for further preparation and analyses in the laboratory.

From bulk BA and FA samples, the following particle size fractions were separated by sieving. BA fractions: >2 mm, 1-2 mm, 0.6-1.0 mm, 0.5-0.6 mm, 0.4-0.5 mm, 0.2-0.4 mm, 0.1-0.2 mm, 0.08-0.1 mm and <0.08 mm; FA fractions: >0.1 mm, 0.09-0.1 mm, 0.08-0.09 mm, 0.071-0.08 mm, 0.063-0.071 mm, 0.056-0.063 mm, 0.053-0.056 mm, 0.050-0.053 mm, 0.045-0.050 mm, 0.036-0.045 mm, 0.032-0.036 mm and <0.032 mm (percentage yields are given in Tables 1 and 2).

Table 1. Yields (%) and concentrations (in wt %) of target compounds and elements in BA fractions (mm).

–	>2	1-2	0.6-1.0	0.5-0.6	0.4-0.5	0.2-0.4	0.1-0.2	0.08-0.10	<0.08	Bulk BA
Yield (%)	14.52	20.14	13.97	5.89	6.3	20.82	14.11	1.78	2.47	100
Na ₂ O	0.15	0.11	0.12	0.12	0.14	0.17	0.21	0.12	0.01	0.14
MgO	1.01	1.02	1.02	1.01	1.02	1.05	1.14	1.1	0.88	1.04
Al ₂ O ₃	28.97	22.74	23.05	22.59	24.58	25.9	24.33	15.82	8.92	24.21
SiO ₂	54.32	44.71	44.97	44.19	47.36	49.34	45.70	30.73	15.51	46.41
P ₂ O ₅	0.085	0.118	0.124	0.125	0.028	0.137	0.181	0.180	0.074	0.122
K ₂ O	1.74	1.43	1.38	1.34	1.49	1.71	1.85	1.24	0.39	1.55
CaO	2.45	15.76	15.13	15.79	12.28	9.87	12.87	26.92	46.22	12.84
TiO ₂	1.62	1.30	1.33	1.33	1.45	1.52	1.55	1.21	0.54	1.42
MnO	0.034	0.029	0.032	0.041	0.042	0.052	0.071	0.085	0.053	0.044
Fe ₂ O ₃	2.97	2.98	3.09	3.35	3.29	3.56	3.79	4.45	4.13	3.33
SO ₃	0.86	5.97	6.45	7.06	5.38	4.15	5.54	12.63	18.3	5.30
As	0.0005	0.0055	0.0067	0.0105	0.0093	0.0098	0.0198	0.0417	0.0660	0.0105

Table 2. Yields (%) and concentrations (in wt %) of target compounds and elements in FA fractions (mm).

–	>0.1	0.09-0.1	0.08-0.09	0.071-0.08	0.063-0.071	0.056-0.063	0.053-0.056	0.050-0.053	0.045-0.050	0.036-0.045	0.032-0.036	<0.032	Bulk FA
Yield	11.93	5.17	7.16	10.54	4.77	12.72	17.69	5.17	3.78	12.52	4.57	3.98	100
Na ₂ O	0.29	0.31	0.29	0.29	0.30	0.32	0.31	0.31	0.31	0.31	0.31	0.31	0.30
MgO	1.49	1.58	1.58	1.55	1.60	1.63	1.64	1.67	1.66	1.64	1.63	1.55	1.60
Al ₂ O ₃	25.61	24.54	24.38	24.43	24.13	24.09	23.53	23.34	22.94	23.22	23.47	23.22	23.10
SiO ₂	44.53	42.43	42.27	42.46	41.53	41.34	40.74	40.34	39.65	40.07	40.48	40.45	41.52
P ₂ O ₅	0.353	0.395	0.391	0.383	0.401	0.417	0.409	0.405	0.402	0.394	0.392	0.362	0.393
K ₂ O	1.65	1.50	1.51	1.44	1.40	1.36	1.34	1.33	1.31	1.30	1.31	1.31	1.40
CaO	10.72	12.13	12.44	12.32	12.82	12.71	13.23	13.63	14.23	13.89	13.58	13.07	12.79
TiO ₂	1.94	1.99	1.95	1.9	1.95	1.89	1.96	2.02	1.98	1.92	1.92	1.85	1.94
MnO	0.144	0.172	0.165	0.167	0.182	0.181	0.204	0.221	0.221	0.204	0.205	0.192	0.186
Fe ₂ O ₃	5.72	6.52	6.32	6.51	6.79	7.02	7.45	7.52	7.88	7.61	7.4	7.27	6.96
SO ₃	3.94	4.37	4.68	4.35	4.57	4.51	4.5	4.68	4.93	4.87	4.72	4.48	4.51
As	0.0526	0.0681	0.0645	0.0641	0.0741	0.0730	0.0841	0.0962	0.0985	0.0924	0.0863	0.0803	0.0763

In order to distinguish between CaO and Fe₂O₃ associations, non-magnetic / magnetic fractions of BA and FA were analyzed for target compounds and elements. Due to quite different granulometry of BA (coarse grains) and FA (fine particles), similar particle-size fractions of BA (0.1-0.2 mm) and FA (> 0.1 mm) were used for the magnetic separation. Magnetic concentrates were manually separated (when dry) using a magnet.

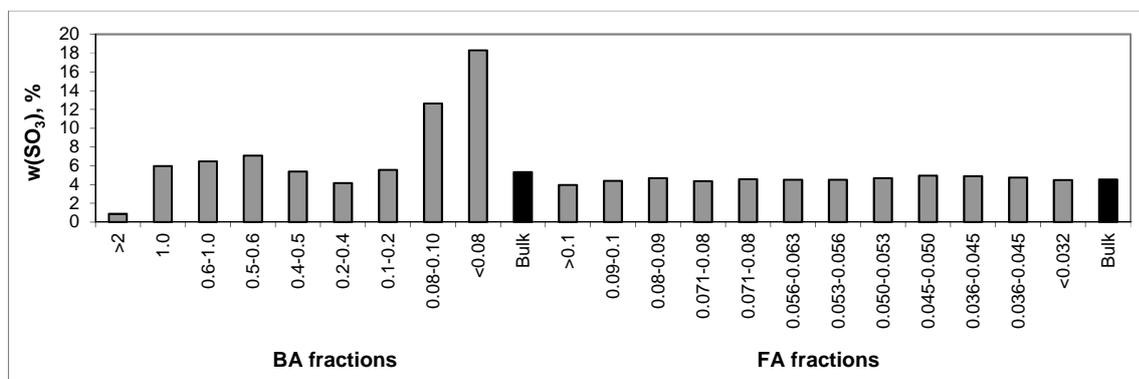
The samples of BA and FA were milled using vibration mill Retsch MM400 and (using binding additive Boreox) 40 mm pellets were pressed on Vaneox automatic press. The elemental analysis was conducted on wavelength-dispersive X-ray fluorescence spectrometer ARL PERFORM'X 4200 W (Switzerland) equipped with 2 detectors, 9 crystals and 4 collimators.

3. RESULTS AND DISCUSSION

3.1. Concentrations of Elements in Ash Fractions

Chemical analysis of particle-size fractions of BA is given in Table 1 and the same data for FA are listed in Table 2. Unlike FA, elemental concentrations in BA fractions exhibit a wide range: CaO and SiO₂ concentrations vary from 2 to 46% and from 15 to 54%, respectively. The considerable differences in the coarser and finer fractions were brought about by adding limestone as a desulphurization additive. For the effective retention of S, limestone was finely ground while SiO₂ (and some aluminosilicates) originated from relatively larger grains. Therefore, finer fractions are highly enriched in CaO while coarse fractions contain much more SiO₂. Unlike BA, the CaO and SiO₂ concentrations in FA vary “only” from 10.72 to 14.23% and from 39.65 to 44.53%, respectively.

For easier evaluation, the distribution trends of As and S are depicted in Figs. (1 and 2) showing higher concentrations of As in FA fractions and some increase in finer fractions of BA. Such behaviour corresponds with volatile character of As. The highest S concentrations are present in the finer BA fractions.

**Fig. (1).** Distribution of SO₃ within particle-size fractions of BA and FA.

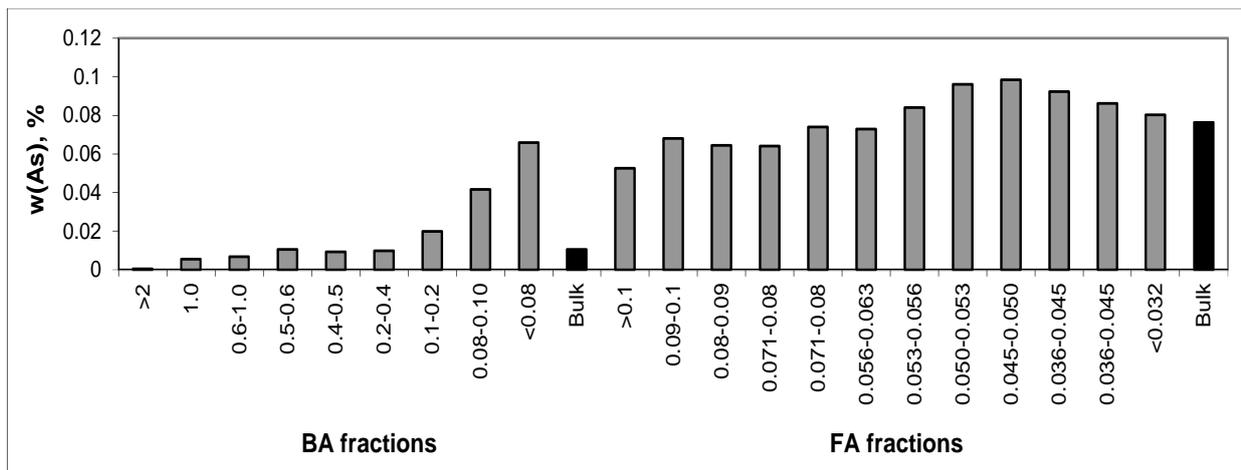


Fig. (2). Distribution of As within particle-size fractions of BA and FA.

3.2. Relationships Between Concentrations of Target Elements

Partitioning of As and S within particle size fractions was evaluated in terms of distribution of the major element oxides, namely CaO and Fe₂O₃.

3.2.1. Sulphur

Relationships between concentrations of SO₃ and those of CaO and Fe₂O₃ are depicted in Fig. (3) for BA and in Fig. (4) for FA fractions.

Figs. (3 and 4) clearly document that SO₃ is predominantly associated with CaO both in BA and in FA fractions. The effect of Fe₂O₃ on SO₃ distribution is of less significance in these samples.

Association of SO₃ with CaO documents the efficient retention of sulphur at coal combustion, which is usually explained through the reactions see equation (1) and (2) [30]:

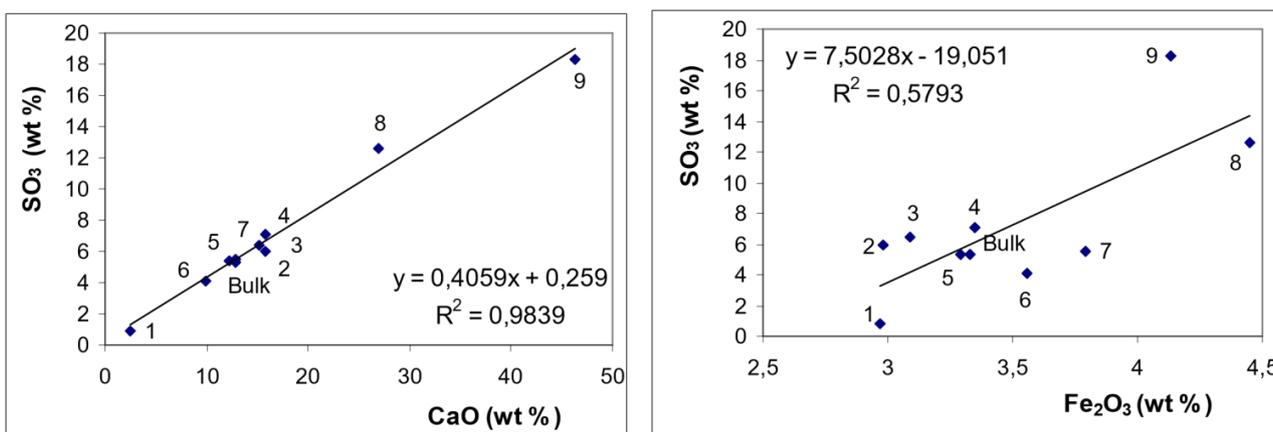


Fig. (3). Concentrations of SO₃ vs. CaO and Fe₂O₃ in each particle-size fraction of BA studied. The fractions were numbered in the order of decreasing particle size: (1) >2 mm, (2) 1-2 mm, (3) 0.6-1.0 mm, (4) 0.5-0.6 mm, (5) 0.4-0.5 mm, (6) 0.2-0.4 mm, (7) 0.1-0.2 mm, (8) 0.08-0.1 mm and (9) <0.08 mm.

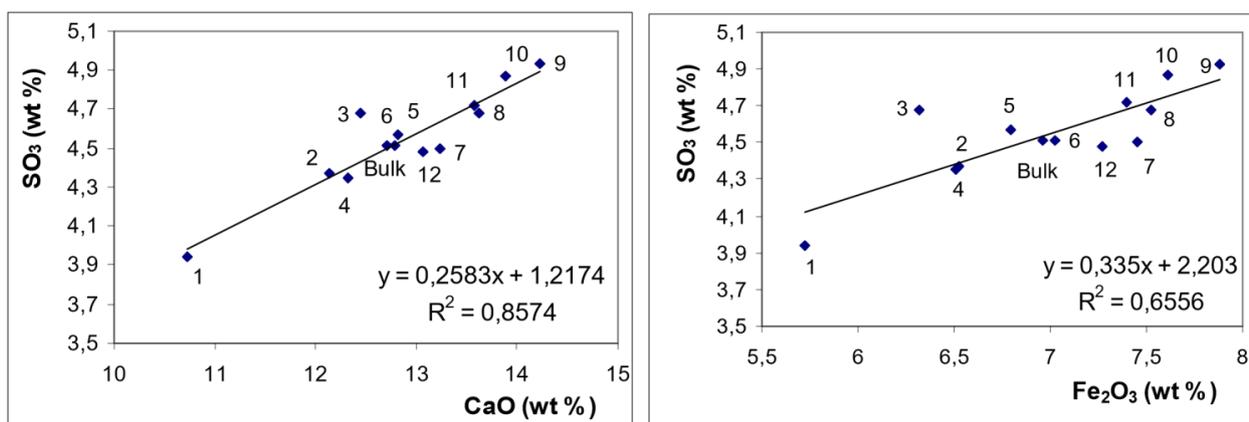


Fig. (4). Concentrations of SO₃ vs. CaO and Fe₂O₃ in each particle-size fraction of FA studied. The fractions were numbered in the order of decreasing particle size: (1) >0.1 mm, (2) 0.09-0.1 mm, (3) 0.08-0.09 mm, (4) 0.071-0.08 mm, (5) 0.063-0.071 mm, (6) 0.056-0.063 mm, (7) 0.053-0.056 mm, (8) 0.050-0.053 mm, (9) 0.045-0.050 mm, (10) 0.036-0.045 mm, (11) 0.032-0.036 mm and (12) <0.32 mm.

3.2.2. Arsenic

Mutual relationships (correlations) between the concentrations of As and those of CaO and Fe₂O₃ are shown in Fig. (5) for BA and in Fig. (6) for FA fractions.

While the behaviour of S (in BA and FA) is quite straightforward (indicating dominant affinity to CaO), the distribution of As exhibits good correlations with both CaO and Fe₂O₃. It can be seen from Figs. (5 and 6) that in BA, the correlation with CaO is more significant while in FA, the correlation coefficient for Fe₂O₃ is slightly higher.

In order to distinguish between CaO and Fe₂O₃ associations, non-magnetic / magnetic fractions of BA and FA were analyzed for target compounds and elements (Table 3). For easier comparison and evaluation, the concentrations of the key compounds and elements are plotted in (Fig. 7).

Table 3. Concentrations (wt %) of target compounds and elements in magnetic and non-magnetic concentrates of BA and FA.

-	BA 0.1-0.2 mm		FA >0.1 mm	
	Non-magnetic	Magnetic	Non-magnetic	Magnetic
Na ₂ O	0.20	0.22	0.29	0.28
MgO	1.12	1.59	1.47	1.45
Al ₂ O ₃	24.45	21.38	25.65	25.56
SiO ₂	46.06	36.03	44.6	44.28
P ₂ O ₅	0.186	0.120	0.350	0.353
K ₂ O	1.89	1.27	1.65	1.60
CaO	13.18	4.05	10.77	10.58
TiO ₂	1.55	0.90	1.93	1.90
MnO	0.060	0.313	0.143	0.149
Fe ₂ O ₃	2.98	28.59	5.62	6.28
SO ₃	5.60	1.37	4.01	3.77
As	0.0205	0.0145	0.0517	0.0575

The composition of magnetic concentrates and the residues after magnetic separation Table 3, Fig. (7) show (as expected) that higher concentrations of CaO were present in non-magnetic fractions and higher concentrations of Fe₂O₃ in magnetic fractions in both BA and FA. Data summarized in Table 3 and depicted in Fig. (7) reveal that SO₃ exhibits higher concentrations of fractions with higher CaO content. However, the behaviour of As differed in BA and FA; in BA it followed the distribution of CaO while in FA higher concentration, was related to the fraction with higher Fe₂O₃ (and lower CaO) content.

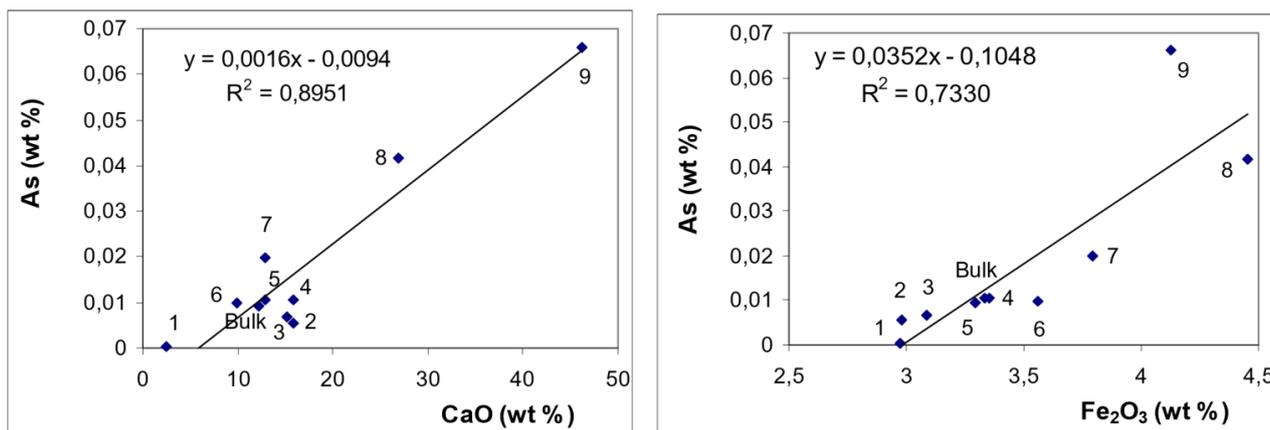


Fig. (5). Concentrations of As vs. CaO and Fe₂O₃ in each particle-size fraction of BA studied. The fractions were numbered in the order of decreasing particle size: (1) >2 mm, (2) 1-2 mm, (3) 0.6-1.0 mm, (4) 0.5-0.6 mm, (5) 0.4-0.5 mm, (6) 0.2-0.4 mm, (7) 0.1-0.2 mm, (8) 0.08-0.1 mm and (9) <0.08 mm.

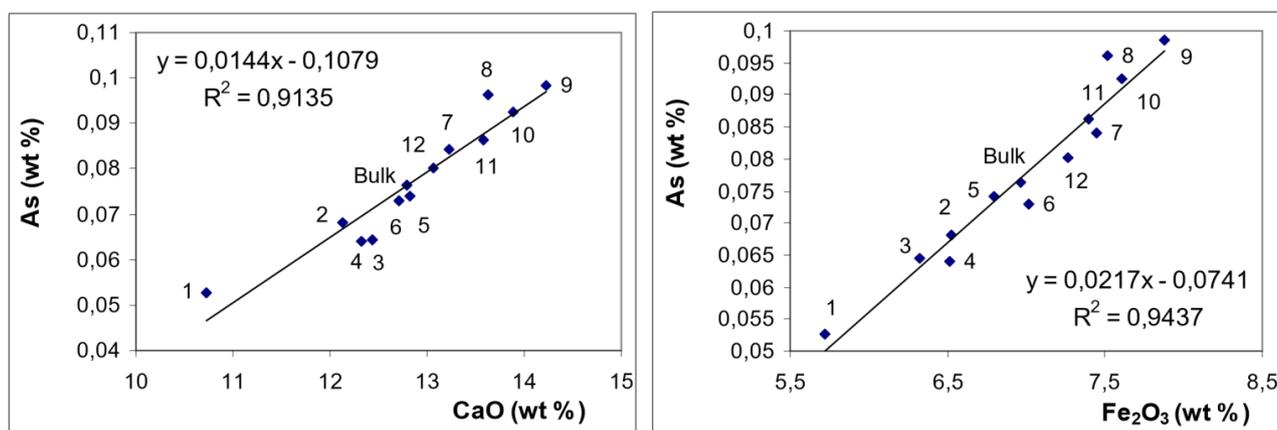


Fig. (6). Concentrations of As vs. CaO and Fe₂O₃ in each particle-size fraction of FA studied. The fractions were numbered in the order of decreasing particle size: (1) >0.1 mm, (2) 0.09-0.1 mm, (3) 0.08-0.09 mm, (4) 0.071-0.08 mm, (5) 0.063-0.071 mm, (6) 0.056-0.063 mm, (7) 0.053-0.056 mm, (8) 0.050-0.053 mm, (9) 0.045-0.050 mm, (10) 0.036-0.045 mm, (11) 0.032-0.036 mm and (12) <0.32 mm.

The observations revealed from magnetic / non-magnetic fractions are consistent with those inferred from the correlation coefficients: in BA As exhibits dominant association with CaO while in FA the affinity to Fe₂O₃ is slightly more significant.

The association between As and CaO was described (i.a.) by Clemense *et al.* [30], López-Antón *et al.* [34] or Liu *et al.* [35]. The most abundant specie resulting from As-Ca interaction is Ca₃(AsO₄)₂ [36 - 39] and the corresponding reaction equations (3) and (4) are as follows [30, 33, 40 - 42]:



Thermodynamic equilibrium calculations revealed that FeAsO₄ was dominant stable specie during As-Fe interaction [32]. Possible chemical reactions between As and Fe were presented in equation (5) (e.g.) by López-Antón *et al.* [11].



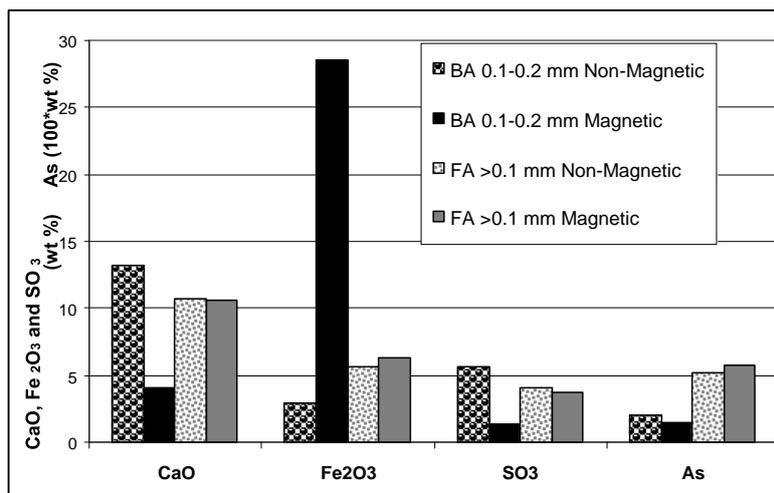


Fig. (7). Distribution of As within particle-size fractions of BA and FA.

The latest detailed review on As behaviour and retention during coal combustion (published in 2018) concluded that both Fe and Ca could provide sites for As association [43], which is consistent with the results presented in Figs. (5 and 6) and with similar reactivities of As to Ca and Fe reported by Seames and Wendt [31] (provided both active sites are available).

However, there is no generally supported conclusion which As association is more significant and which conditions are preferred. For example, laboratory-scale As retention experiments with various Fe and/or Ca contents [45 - 47] lead to the conclusion that As was preferentially associated with Fe. Herein, Figs. (5 and 6) indicate that preferential association of As to Fe was observed only in FA. It is interesting to note in this context that according to Zielinski *et al.* [44], important affecting parameter is alkalinity/acidity of the studied ash - alkaline ashes promote As-Ca association whereas As-Fe association prevails in acidic ashes. Zhou *et al.* [46] concluded predominant As-Fe association during laboratory-scale experiments where similar concentrations of Fe and Ca were used, which is quite different from the conditions in this study. Herein (Figs. 5 and 6), the concentrations of CaO in (bulk) BA and FA was nearly the same (12.84 and 12.79%) whereas the contents of Fe₂O₃ in BA and FA was 3.33% and 6.96% (there was a twofold increase in FA in comparison with BA). Better availability of Fe active sites in FA might have resulted in less significant As-Ca association. Since the magnetic fraction of FA contains also higher MnO content, this effect cannot be excluded as well. Nevertheless, it is interesting to note that the significance of As-Ca and As-Fe associations in BA and FA is still comparable, despite the fact that the content of Fe₂O₃ in BA and FA is significantly lower than that of CaO.

Temperature is another important parameter affecting As retention [37]. The adsorption of As on FA components is believed to be a combination of chemical and physical adsorption. Even though the effect of temperature is quite complicated, it is widely accepted that the dominant process in higher temperature regions is chemisorption [43]. However, the thermodynamically predicted behaviour can occur only if there is no kinetic limitation (*e.g.*, rapid flue gas cooling) [40, 48]. Therefore, this effect can be another possible reason of the differences in As behaviour in BA and FA.

In addition to the aforementioned reasons, grain-size effect should be mentioned in this context as well. Nevertheless, typical physical condensation on the finest FA particles is quite unlikely in these samples because As concentrations in the finest FA fractions are lower than those in medium size fractions.

CONCLUSION

Possible relationships between the concentrations of S and As and the contents of CaO and Fe₂O₃ were evaluated in BA and FA fractions from a fluidised-bed power station.

The dominant association of SO₃ was with CaO, which corresponds with efficient desulphurization using desulphurization additive, such as limestone. In contrast, As exhibited association with both CaO and Fe₂O₃ - CaO correlation was more significant in BA while Fe₂O₃ correlation slightly prevailed in FA. The difference in As behaviour in BA and FA could correspond (*e.g.*) with bulk ash composition (concentration of Fe₂O₃ in FA is twofold higher than that in BA) or grain-size effect.

The results document that not only (widely accepted) Ca-bearing additives but also Fe-based ash components can be used for efficient decreasing toxic As emissions from coal-fired power stations.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The author declares no conflict of interest, financial or otherwise.

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