Reuse of waste ashes formed at oil shale based power industry in Estonia

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Abstract

Estonian oil shale belongs to low-grade fossil fuels and by its combustion huge quantities of ash (currently about 5 million tons annually) are formed. Since 1959 pulverized firing (PF) has been used, and circulating fluidized bed combustion (CFBC) technology has recently been implemented – two units each of 215 MW capacity are in operation. In previous investigations of PF ashes the results have been used as a basis for several large-scale applications like production of construction materials and conditioning/neutralizing of soils; a developing of industrial applications for CFBC ashes is hindered by insufficient basic data. In the current investigation attention was focused on the reactivity of ashes towards SO_2 and CO_2 in heterogeneous gas – solid and gas – water – solid systems, being important for characterization of ashes as sorbents for the capture of acidic gases named from flue gases. The significant differences in chemical and phase composition as well as in surface properties of ashes have been shown. The SO_2-binding characteristics for CFBC ashes are higher than for PF ashes and they have more perspective as dry sorbents of sulphur dioxide. Also, under wet carbonization conditions, CFBC ashes can be carbonized more deeply as compared to PF ashes. As a result of carbonation, ashes could be environmentally friendly landfilled and abatement of CO_2 emissions will be achieved.
Keywords: Estonian oil shale, pulverized firing, circulating fluidized bed combustion, waste ashes, reactivity, sulphur dioxide, carbon dioxide.

1   Introduction

Estonian power supply is over 90% covered by oil shale fired thermal power plants. Local solid fossil fuel oil shale is characterized by low heating value

(8.3-8.5 MJ/kg), moderate moisture content (10-13%), high content of minerals (60-65%) and by the unique and complicated chemical and mineralogical composition of last one. Mineral matter of the Estonian oil shale consists mainly of two components: carbonate matter and sandy-clay matter [1]. In the course of combustion, fuel inorganic part undergoes several chemical transformations, from decomposition processes to the formation of new secondary mineral compounds and phases at higher temperatures.

The mechanism of the processes that take place during pulverized firing (PF) of oil shale, including the formation of ash deposits at heat-transfer surfaces, is thoroughly examined by Ots [1], Ots *et al.* [2]. Investigations of fly ash composition and reactivity brought about developing and introducing ash-recycling processes like production of various building materials, cement with special properties and other products (Kikas [3]). Ash is also utilized as an expedient material in road construction as well as soil conditioner in agriculture (Kärblane [4]) and as a neutralizing additive in the production of mineral fertilizers (Veiderma *et al.* [5]). In addition, it could be used as a SO_2 and CO_2 sorbent (Trikkel [6], Kuusik *et al.* [7]).

Compared to PF, in the case of circulating fluidized-bed combustion (CFBC) the operating temperatures are considerably lower. Consequently, chemical and phase composition of CFBC waste ashes differ noticeably (Kuusik *et al.* [8]) and that is why the differences in chemical reactivity can also be expected.

The aim of the current study was to elucidate chemical reactivity of CFBC ashes compared to PF ones in the systems that are important in the formation of ash deposits in a boiler, at ash deposition at landfill, at flue gas desulphurization as well as at reducing CO_2 emissions.

2 Materials and methods

Ash samples used were collected from different points of the ash-separation systems of CFBC and PF boilers at the Estonian Thermal Power Plant. The CFBC ashes studied were bottom ash (CFBC/BA), intrex ash (CFBC/INT), economizer ash (CFBC/ECO), air preheater ash (CFBC/PHA), electrostatic precipitator ash from fields 1 and 4 (CFBC/ESPA 1 and 4) and mixture of ashes (CFBC/Mix) taken from a common ash silo where the ash from different units is collected before landfilling on ash fields. The PF ashes used were bottom ash (PF/BA), superheater ash (PF/SHA), economizer ash (PF/ECO), cyclone ash (PF/CA) and electrostatic precipitator ash from fields 1 and 3 (PF/ESPA 1 and 3). Chemical and phase composition as well as physical properties of these ashes are presented in Table 1 and discussed in more detail in paper of Kuusik *et al.* [8].

Reactivity of ashes towards SO_2 or CO_2 was tested in a heterogeneous gas-solid system using thermogravimetric equipment (Q-derivatograph, MOM) under isothermal conditions. In both cases the temperature of the isothermal experiment was 700°C, partial pressure of SO_2 or CO_2 was 190 and 144 mm Hg, respectively. The samples (100 ± 0.5 mg) were heated up to 700°C in air with heating rate of 10 K/min. The gas mixture was then fed into the furnace with the

rate of 270 ml/min. The thickness of the sample layer in multiplate Pt crucibles was about 0.2–0.3 mm. To study the effect of grinding on SO_2- and CO_2-binding, the initial samples (except for CFBC/BA, which was slightly crushed to pass the 630 μm sieve) and the ground ones were used. Samples were ground in a one-ball vibration mill until the majority (approx. 85–100%) passed through the 45 μm sieve. In some experiments with CO_2, samples were heated up to 900°C to achieve full decomposition of carbonates and then cooled to 700°C to perform isothermal binding.

To characterize high-temperature binding of SO_2 and CO_2 by ashes, the following parameters were calculated:

SO_2- or CO_2-binding capacity (*BC*; weight of SO_2 or CO_2 bound by 100 mg of sample),
SO_2- or CO_2-binding rate (*W*; mg SO_2 or CO_2 per mg sample·min^{-1}),
SO_2- or CO_2-binding efficiency, (*BE*, %) showing the extent of utilization of CaO and MgO contained in the sample

The parameters were calculated on the basis of experimental and analyses data and the following summary binding reactions:
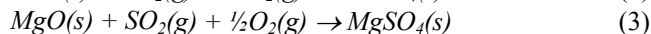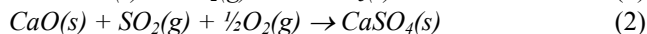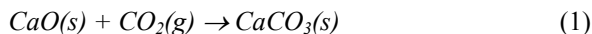
$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \tag{1}$$
$$CaO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CaSO_4(s) \tag{2}$$
$$MgO(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow MgSO_4(s) \tag{3}$$

Table 1:   Chemical composition and physical properties of CFBC and PF ashes.

ASH	Content (%)							d_{mean} μm	SSA m^2/g
	CaO_t	CaO_f	MgO_t	CO_2	S_t	$S_{sulfate}$	$S_{sulfide}$		
CFBC/BA	49.39	12.48	9.25	15.14	4.53	4.32	0.10	197	2.06
CFBC/INT	47.59	18.87	13.65	1.23	7.76	7.70	0.02	95	2.61
CFBC/ECO	32.84	10.40	9.50	5.48	2.32	2.22	0	27	6.89
CFBC/PHA	35.17	12.26	10.77	4.30	3.31	3.27	0.0013	32	5.40
CFBC/ESPA1	29.52	8.45	8.33	4.60	1.71	1.71	0	25	8.00
CFBC/ESPA4	28.88	2.82	9.35	3.80	2.23	2.21	0	23	7.92
CFBC/Mix	33.28	10.33	9.50	6.41	2.46	2.43	0.03	28	7.11
PF/BA	50.75	24.84	15.19	2.75	1.27	1.27	0	115	1.75
PF/SHA	54.71	23.08	7.81	0.96	1.98	1.93	0	105	0.50
PF/ECO	48.00	16.04	8.24	2.50	2.52	2.52	0.006	53	0.44
PF/CA	49.39	22.52	14.19	0.70	1.33	1.33	0	48	0.36
PF/ESPA1	36.08	13.56	11.26	1.16	2.74	2.74	0	24	0.61
PF/ESPA3	26.85	5.98	5.98	0.80	3.67	3.67	0	23	1.09

Carbonization of aqueous suspensions of ash with model gas, whose composition (10% CO_2 and 90% air) simulated CO_2 content of flue gases formed

at oil shale combustion, was carried out in an absorber (diameter 55 mm, water column height 500 mm) equipped with magnetic stirrer for achieving a better interfacial contact and a sintered glass gas distributor (pore diameter 100 μm). The experiment was carried out until suspension pH reached 7.5. Then the suspension was filtered and solid residue dehumidified at 105°C. For the liquid phase, Ca^{2+} content (Vilbok [9]), TDS (total dissolved solids) and alkalinity [10] were determined. For the solid residue the content of free CaO (Reispere [11]) and CO_2 and pH of aqueous suspension of solid residue [12] were determined.

3   Results and discussion

Free CaO is the main binder of SO_2 and CO_2 in the ashes (Reactions 1 and 2). Although MgO does not take part in CO_2 binding under these conditions [13], it has a certain role in SO_2 binding (Kaljuvee *et al.* [13, 14]). Hence, the negative influence of coarser fractional composition of the samples and, correspondingly, the lower level of specific surface area (SSA) in the case of, for example, CFBC/BA (mean particle size 197 μm; SSA 2.1 m^2/g) and CFBC/INT (95 μm; 2.6 m^2/g) should be compensated by higher level of free CaO content – 11.9 and 18.9%, respectively (see Table 1).

PF/BA and PF/CA are both characterized by a quite high content of free CaO (23–25%), but they differ noticeably (5 times) in their SSA. PF/ESPA1 is characterized by fine fractional composition (d_{mean} = 24 μm), low content of free CaO, and despite a small particle size by a low value of SSA (0.61 m^2/g) and should show a modest binding activity. CFBC/ECO and CFBC/PHA are somewhere in the middle of the scale considering these parameters.

3.1 Transformations in the Gas-Solid System SO_2-Ash

After 30 minutes of the contact between solid and gaseous phases, SO_2-binding capacity of different CFBC ashes was about 26–30 mg SO_2 per 100 mg sample. 55–70% of this value was achieved during the first 2-min contact already (Fig. 1).

BC values for PF ashes differed from each other more considerably – from 10.4 to 23.1 mg SO_2 per 100 mg sample – being the highest for PF/ESPA1. During a 2-min contact, PF/BA bound 58%, while PF/ESPA1 and PF/CA only 33% of the total amount of bound sulphur dioxide. This data correspond to the data obtained in our earlier research (Kaljuvee *et al.* [13, 14]) and can be explained by the differences in chemical and fractional composition as well as in physical and chemical properties of the ashes. Thus, CFBC/BA and CFBC/INT have coarser fractional composition and lower SSA level, but higher free CaO content, while CFBC/ESPA has fine fractional composition (and high level of SSA), but low content of free CaO (see Table 1). Differences in *BC* values for PF/BA and PF/CA can be explained by their different SSA values (1.75 and 0.36 m^2/g, respectively).
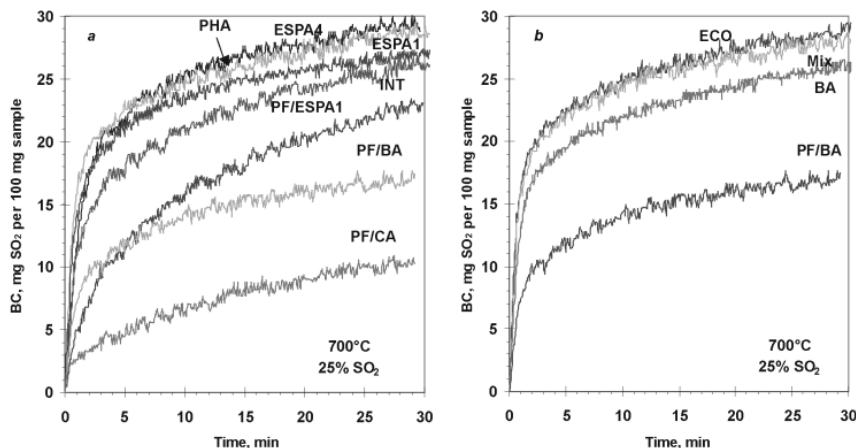
Figure 1: SO_2-binding capacity (*BC*) of the ashes.

In the experiments of SO_2-binding MgO, free CaO and, partially, Ca-silicates can take part in the reactions with SO_2. So, in this case binding efficiency, *BE* was calculated on the basis of total content of CaO and MgO in the sample – *BE(CaO·MgO)*. *BE(CaO·MgO)* values indicated the highest level of utilization of both oxides for ESPA4 (74%) and the lowest for BA and INT – about 41% (Fig. 2) BA was the most active among PF ashes, having an average SO_2-binding rate 0.10 mg SO_2 per mg sample $\cdot$ min^{-1}. Like other indicators of SO_2-binding ability, the values of *BE(CaO·MgO)* for PF ashes were much less than those for CFBC ashes: 46.9% (the highest) for ESPA1, 25.7% for BA and 15.4% for CA (Fig. 2).

For all the ashes studied preliminary grinding (up to grain size -45 μm) increased their binding ability. In general, it was noticed that for the ashes characterized by coarse fractional composition (CFBC/BA, CFBC/INT, PF/BA) and/or those having been allocated to high temperatures at PF (especially PF/CA) resulting in the formation of liquid phases hindering further diffusion of SO_2 into the particles.

Thus, grinding increased the *BC* and *BE* values for PF/CA 2.2 times, for CFBC/BA, CFBC/INT and PF/BA 55–70%, for CFBC/ECO and CFBC/PHA 20–30%, for CFBC/ESPA1 and PF/ESPA1 10–20%, and for CFBC/ESPA4 there was no change in these values. Among ground CFBC ashes, *BC* value was the highest for BA and INT (40–42 mg SO_2 per 100 mg sample), *BE* value for ECO –81.5% (Fig. 2). Among PF ashes, *BC* value was the highest for BA –30.2 mg SO_2 per 100 mg sample and *BE* value for ESPA1 –50.6 % (see Fig. 2).

These results are in good correlation with the increase in the SSA of the samples: for PF/CA 4.4 times (from 0.36 m^2/g to 1.45 m^2/g), for CFBC/BA, CFBC/INT, and PF/BA 1.5–2.3 times, for the other ashes on the level of 1.1 times, except for CFBC/ESPA4 and PF/ESPA1, for which even a small decrease in the SSA was observed. Comparing these results with those obtained with

Karinu limestone, the *BC* values of the more active ashes (CFBC/BA and INT) were only 1.4 times less, but the *BE* value of CFBC/ECO was on the same level than that of Karinu limestone (see Fig. 2).
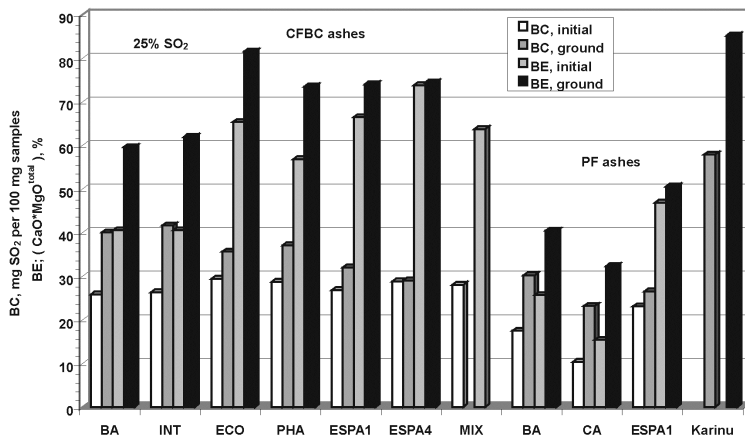

Figure 2: The influence of grinding on SO_2-binding capacity (*BC*) and efficiency (*BE/CaO·MgO*) at 700°C after 30-min contact.

3.2 Transformations in the gas–solid system CO_2–ash

CO_2-binding capacities of the ashes stay between 1 and 13 mg CO_2/100 mg (Fig. 3). Among CFBC samples, the highest binding capacity was calculated for bottom ash. Binding capacities of ECO, PHA and Mix were about 5 mg CO_2/100 mg, the lowest *BC* values were of INT and ESPA. Bottom ash of pulverized firing bound also about 5 mg of CO_2 per 100 mg sample; binding capacities of PF/CA and PF/ESPA were low.

Grinding of CFBC samples decreased their binding capacities noticeably, except for INT. Decrease in *BC* was from 12% (BA) to 60–70% (ECO, PHA and ESPA). This phenomenon is specific of CFBC samples, because *BC* of ground PF samples is about 75–85% higher as compared to the initial ones. This correlates with the increase in specific surface area, which is 4 times higher for ground PF/CA and 1.5 times higher for ground PF/BA. However, grinding increased also SSA of CFBC ashes. The decrease in *BC* was less for BA and INT, also the increase in SSA during grinding was higher for these samples – 2.3 and 1.6 times, respectively.

The effect of decarbonization temperature on *BC* was even more severe – the decrease in *BC* for the samples heated before binding to 700°C and 900°C was 67% – from 5.5 to 1.8 mg CO_2/100 mg.

Separate experiments were performed to estimate changes in SSA and CaO_f content during pre-treatment. It was found that a 30-min grinding increased SSA from 5.3 to 7.7 m^2/g, but heating of this ground sample to 900°C decreased its SSA to 3.1 m^2/g. Also the level of free CaO decreased remarkably during heating. Presumably, some secondary reactions take place during heating that reduce free CaO content in CFBC ashes being more intensive at higher temperatures.
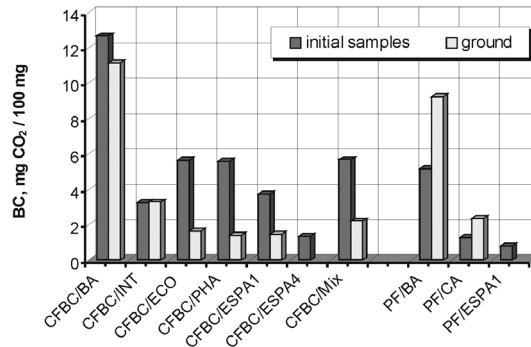

Figure 3: CO_2-binding capacities (BC) of the initial and ground to particle size less than 45 μm ash samples after 30-min binding.

Thus, as compared to PF ashes, CO_2 binding capacities of CFBC ashes are 2-3 times higher. The best results were obtained in both cases with bottom ashes. The method of grinding used improved noticeably binding parameters of PF ashes and reduced those of CFBC ashes. According to the results obtained, it can also be concluded that intensive contamination of heating surfaces in CFB boilers with secondary carbonaceous deposits should not be a serious problem.

3.3 CO_2-Ash-Water System

To characterize CO_2-binding in ash–water suspensions the following parameters were used. Carbonization extent was described by index N indicating the excess of the CO_2 amount entrained into suspensions over the stoichiometric ratio calculated according to Equation (1). Effectiveness of the carbonization process was described by the CO_2-binding degree (BD_{CO2}). BD_{CO2} shows which part of the theoretical ash-binding capacity is utilized. It was calculated basing on the changes in CO_2 content:

$$BD_{CO2} = \frac{CO_2}{CO_{2\,max}} \cdot 100 \ \% \qquad (4)$$

CO_2 is analytically determined CO_2 content of the sample (%)

$CO_{2\,max}$ is the maximal possible CO_2 content of the sample (%), calculated on the basis of content of free or total CaO in the initial sample as follows:

$$CO_{2max} = \frac{CaO^i \cdot M_{CO_2} / M_{CaO} + CO_2^i}{100 + CaO^i \cdot M_{CO_2} / M_{CaO}} \cdot 100 \quad \%\qquad(5)$$

CaO^i and CO_2^i denote the content (%) of free or total CaO and CO_2 in the initial sample, respectively.

The results obtained are presented in Figure 4. Chemical analysis of the liquid phase indicated that after carbonization the suspensions of both kinds of ashes contain small amounts of alkaline components. In the suspensions of CFBC ashes, content of Ca^{2+} ion is near saturation point or even higher (in the case of intrex ash 1110 mg/l). In the suspensions of PF ashes, the concentrations of Ca^{2+} ions stay on a noticeably lower level (240–590 mg/l). The TDS values were proportional to the content of Ca^{2+} ion.
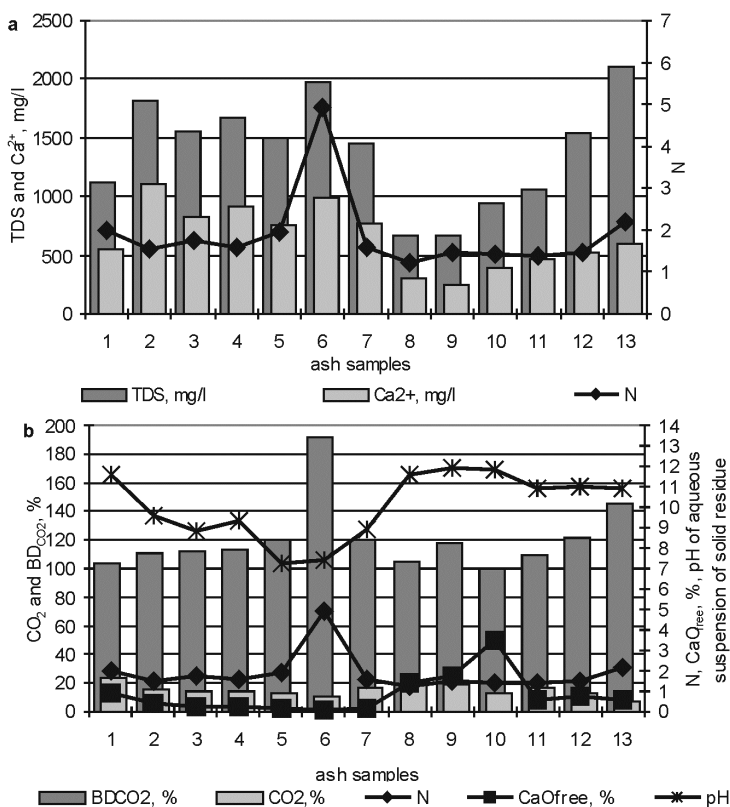

Figure 4: Ca^{2+} and TDS contents in suspensions of CFBC and PF ashes (a) and characteristics of carbonation process and its final product for CFBC and PF ashes (b): 1-CFBC/BA, 2- CFBC/INT, 3- CFBC/ECO, 4- CFBC/PHA, 5- CFBC/ESPA1, 6-CFBC/ESPA4, 7- CFBC/Mix, 8- PF/BA, 9- PF/SHA, 10- PF/ECO, 11- PF/CA, 12- PF/ESPA1, 13- PF/ESPA3.

Compared to PF ashes, CFBC ashes can be carbonized more deeply accompanied by lowering of pH of the solid residue in most cases below 9 (with the exception of CFBC/BA, full carbonization of which is inhibited due to coarse fractional composition. Higher pH value (10.9–11.9) is elicited by higher content of free CaO (0.57–3.47%) in solid residues of carbonized PF ashes. Apparently, in the case of nonporous PF ashes, some part of free CaO present is not accessible and therefore cannot take part in reaction under these conditions. The content of CO_2 is proportional to that of free CaO and CO_2 in the initial samples (see Table 1). Binding degrees that were calculated basing on content of free CaO in the initial samples were in CFBC and PF ashes predominantly over 100% (104.1–191.3% and 99.9–145.1%, respectively) because there can be other CO_2-binding compounds (MgO, Ca-silicates) present in oil shale ash of heterogeneous composition. In general, for total utilization of free CaO the CFBC ashes need less CO_2 per ton of ash as they contain less free CaO in the initial ash.

4   Conclusions

1) Oil shale ashes formed in boilers operating at different combustion technologies differ by their chemical reactivity towards acidic gases.
2) Sulphation of ashes in model conditions shows that SO_2-binding capacity of CFBC ashes at 700°C remained within a narrow range being the highest for PF/BA. SO_2-binding capacity of CFBC as well as of PF ashes is not completely utilized. Being characterized by a higher binding rate during the initial stage of gas–solid contact, CFBC ashes could be more promising as potential SO_2 sorbents for dry desulphurization of flue gases.
3) Transformations in the gas–solid system CO_2–ash, which are important in evaluating possibilities for formation of calcareous precipitations on heat transfer surfaces in boilers, were investigated. CO_2-binding ability of the ashes at 700°C was relatively low, being 2-3 times higher for CFBC ashes. Within 30 minutes 8–52% of free CaO present in the sample was utilized. According to these data, intensive formation of secondary carbonaceous precipitations on the heat transfer surfaces of the CFB boiler is not foreseen.
4) The results of the experiments on binding gaseous CO_2 by ash–water suspension indicated that, in the same conditions, CFBC ashes could be carbonized more intensively and deeply than PF ashes. Besides lime as a compound of the highest reactivity towards CO_2 also other components like MgO and Ca-silicates present in ash take part in CO_2-binding reactions. Owing to improved CO_2-binding rate, more intensive natural CO_2-mineralization of CFBC ashes as compared to PF ashes in open-air deposits as well as intensive binding of CO_2 from flue gases by aqueous suspension of ash are expected.

Acknowledgements

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