

Definition of mineral and chemical composition of fly ash derived from CFB combustion of coal with biomass

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Objectives

Investigation of chemical and mineralogical composition of fly ash derived from the circulated fluidised bed combustion of Greek lignite, Polish bituminous coal, wood chips and various blends of these feeds.

The characterisation study of the produced fly ash has been accomplished through:

- Chemical analysis such as X-ray fluorescence (XRF) and Inductive Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)
- Particle size distribution (PSD)
- X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) procedures

Analytical methods

The combustion experiments were carried out at the 50 kW lab scale boiler of VTT Technical Research Centre of Finland, and the 12 MW pilot scale boiler of the Chalmers University of Technology (CUT) in Sweden.

Combustion was accomplished at a temperature of 900 °C in both facilities without the use of limestone.

Table 1: Average characteristics and energy contents of the feed fuels

Parameter	Polish Bituminous Coal	Greek lignite	Wood Chips
Proximate analysis			
(wt% dry basis)			
Moisture	1.9	36.5	4.6
Volatiles	29.33	41.67	80.10
Ash	12.96	38.36	1.14
Fixed Carbon	57.71	19.97	18.76
Ultimate analysis			
(wt% dry basis)			
Carbon	68.42	32.29	48.77
Hydrogen	3.91	3.42	5.85
Nitrogen	1.32	1.33	0.45
Oxygen	12.69	17.96	43.79

Sulphur	0.7	1.64	0
Gross Heating Value d. b. (kJ/kg)	29,171	17,887	25,154
Net Heating Value d. b. (kJ/kg)	28,330	17,150	23,899

Results

Classification of the fly ash samples

The analysed ash samples are rich in CaO, while the sum of the oxides Al₂O₃, SiO₂ and Fe₂O₃ is over 50% but less than 70%:

- the fly ashes are classified as class C (ASTM standard), except of sample C1 (lignite) which is associated with class F
- bituminous coal produces fly ash of class C.

Table 2: Classification of the fly ash samples collected at VTT's and CUT's facility

Sample	Composition of feed fuels	Sampling Point/Facility	Al ₂ O ₃ +SiO ₂ +Fe ₂ O ₃	CaO
F1	100% Greek <i>lignite</i>	Fabric Filter/VTT	70.03	12.53
F2	50% Wood Chips-50% Polish Coal	Fabric Filter/VTT	62.65	12.68
F3	100% Wood Chips	Fabric Filter/VTT	56.85	15.04
F4	100% Polish Coal	Fabric Filter/CUT	45.11	8.67
F5	50% Polish Coal - 50% Wood Chips	Fabric Filter/CUT	41.57	18.13
F6	100% Wood Chips	Fabric Filter/CUT	18.46	41.70
C1	100% Greek <i>lignite</i>	Second Cyclone/VTT	80.98	5.73
C2	50% Wood Chips-50% Polish Coal	Second Cyclone/VTT	50.86	14.19
C3	100% Wood Chips	Second Cyclone/VTT	52.72	19.59
C4	100% Polish Coal	Second Cyclone/CUT	27.76	9.58
C5	50% Polish Coal - 50% Wood Chips	Second Cyclone/CUT	33.22	13.76
C6	100% Wood Chips	Second Cyclone/CUT	31.69	41.16

Unburned carbon content

Maximum LOI determined:

- F4 (coal) (32.93%) and C4 (coal) (53.68%)

The ASTM C-618 standard defines:

- upper limit of 6%, concerning class C fly ash utilization as a pozzolan in Portland cement. Good results are obtained by the fly ash samples F1 (lignite), F6 (wood chips) and C1 (lignite), C3 (wood chips).
- SO₃ content should be lower than 5% (only sample C1 (lignite) from the second cyclone)

Chemical composition

- Al_2O_3 occurs in higher amounts in all samples except of F6 (wood chips) and in all samples from the second cyclone.
- The addition of coal in the fuel blend enriches the ash composition in Fe. The oxide Fe_2O_3 was present as hematite or maghemite in almost all samples examined, except of F6 (wood chips) and C6 (wood chips), which contained approximately only 2.5% of Fe_2O_3 .
- Wood fly ash is rich in phosphorous. P_2O_5 was significant enriched in these fly ash samples.
- Calcium is also an important component in wood. Ca levels of fly ash from co-combustion of wood with coal were lower than those of fly ash coming from the combustion of wood solely.
- When the proportion of wood in the coal/wood mixture is increased, the concentration of alkalis (Na and especially K) is also elevated.

Table 3: Ash composition (%) of the samples as determined by XRF-analysis

	F1	F2	F3	F4	F5	F6	C1	C2	C3	C4	C5	C6
SiO₂	40.33	36.58	32.96	23.35	22.81	13.39	47.80	28.05	29.20	14.57	18.72	20.07
Fe₂O₃	8.11	6.53	6.01	6.34	4.69	2.46	9.06	7.70	8.89	4.74	5.53	2.36
Al₂O₃	21.59	19.54	17.88	15.42	14.07	2.61	24.12	15.11	14.63	8.45	8.97	9.26
TiO₂	1.34	1.06	0.90	0.77	0.69	0.03	0.98	0.48	0.39	0.29	0.27	0.05
CaO	12.53	12.68	15.04	8.67	18.13	41.70	5.73	14.19	19.59	9.58	13.76	41.16
MgO	4.10	3.58	4.18	4.71	5.81	8.10	3.64	5.00	5.70	2.99	3.89	4.47
SO₃	8.09	7.51	8.98	3.37	5.86	10.08	3.80	9.65	13.23	3.82	4.81	4.02
P₂O₅	0.71	0.92	1.37	0.87	2.55	4.67	0.50	0.73	1.03	0.31	0.78	2.34
Na₂O	0.30	0.63	1.23	2.17	0.88	2.75	0.28	1.46	1.95	1.10	1.82	0.63
K₂O	2.25	2.05	2.26	1.65	6.41	12.08	3.13	2.23	2.96	0.91	3.07	5.57
LOI	1.10	9.34	9.51	32.93	18.15	2.17	1.19	16.24	2.64	53.68	33.36	10.51
Total	100.35	100.42	100.32	100.25	100.05	100.04	100.23	100.84	100.24	100.44	99.98	100.44

In Table 4 the trace element concentrations determined by ICP-OES are presented:

Table 4: Concentration (mg/kg) of trace elements in the fly ash

	As	Cr	Sample	As	Cr
F1	36±3. 5	190±17	C1	<5	160±13
F2	43±4	182±16	C2	<5	145±15
F3	20±2	180±16	C3	<5	180±16
F4	<5	100±8	C4	<5	32±3
F5	<5	115±9	C5	<5	72±7
F6	<5	29.5±3	C6	<5	20±2
AFBC ash residues form coal combustion [5]	10-300	1-500	AFBC ash residues form coal combustion [5]	10-300	1-500

The concentration of As:

- in lignite fly ash is attributed to the soil parent material, especially the earth crust which is enriched in this element. In these samples the elevated amounts of As could be due to the contact of fly ash with flue gases, the hydraulic conductivity (low in fly ash) and the surface area.

It appears that most of the As in coal is associated with pyrite. In the majority of coals studied, As is primarily associated with massive or late-stage pyrite. In some cases As is associated with fine-grained pyrite and other sulphides.

The concentration of Cr:

- is increasing by increasing O₂ concentration. In addition boiler configuration and operation affect the behaviour of Cr. Lower emissions of Cr are usually detected at lower load. The relatively high concentration of Cr could also be due to the attrition of the power plant equipment and the metallic nozzle of the probe used for sampling. Thus the presence of Cr could be indicative of contamination in association with stainless steel.

Particle Size Distribution

PSD ranges between 1 µm and 200 µm. Moreover a second peak occurs in the size distribution of all samples, in the range between 0.1 and 1 µm.

Samples F1 (lignite), F2 (wood chips/coal), F3 (wood chips) have a coarser particle size than F4 (coal), F5 (wood chips/coal) and F6 (wood chips). This result is due to the different fuel blends used (Figure 1).

The particle size in fly ash from a blend containing wood chips decreases with increasing percentage of this fuel. This is possibly due to the ease of combusting wood chips (Figure 2).

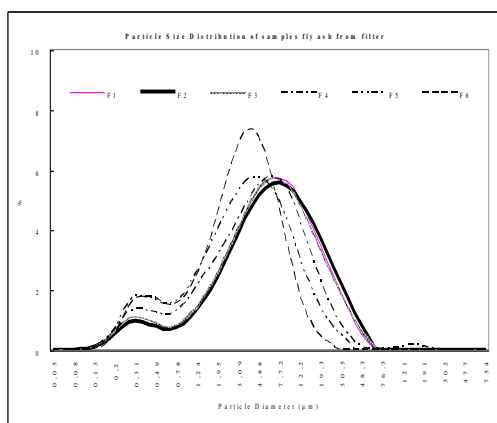


Figure 1: Particle size distribution of samples from fabric filter

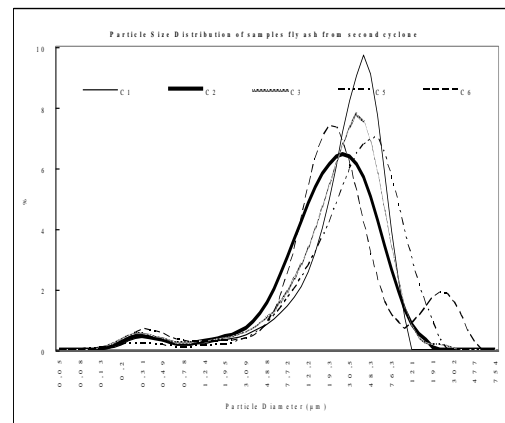


Figure 2: Particle size distribution of samples from second cyclone

X-ray diffraction (XRD)

Evaluating the XRD patterns, several distinct peaks were observed and the following minerals identified:

- quartz, hematite, anhydrite and periclase as well as maghemite, portlandite, gehlenite, magnesioferrite, lime, sylvite and rutile, which occurred in some samples.

Table 5: Mineral phases in the fly ash samples

Mineral Phases	F1	F2	F3	F4	F5	F6	C1	C2	C3	C4	C5	C6
Quartz - SiO ₂	X	X	X	X			X	X	X	X	X	X
Maghemite - Fe ₂ O ₃		X			X		X					
Hematite - Fe ₂ O ₃	X	X	X				X	X	X	X	X	
Anhydrite - CaSO ₄	X	X	X	X			X	X	X	X	X	
Periclase - MgO			X	X	X	X		X	X	X	X	X
Portlandite - Ca(OH) ₂						X			X			X
Gehlenite - Ca ₂ Al(Al,Si) ₂ O ₇					X							
Magnesioferrite - MgFe ₂ O ₄				X								
Lime - CaO						X					X	
Sylvite - KCl						X						
Rutile - TiO ₂	X											

Almost all ash samples contain quartz (primary mineral), especially in cases where ash samples originate from fuels such as bituminous coal and lignite, which contain high amounts of silicon dioxide (Table 3).

The fly ashes from high sulphur coals have higher amounts of iron-bearing minerals compared to the fly ash from low sulphur coals. Formation of iron oxides is partially due to the decomposition of pyrite, which increases the SO_x content of the system and provides the basic cation for nucleation of hematite/magnetite, which then leads to the formation of magnetite microspheres.

Except of quartz, the majority of the samples contain hematite, especially in cases where bituminous coal is used. This type of coal has higher percentages of ferric oxide in comparison with lignite and the wood chips used (Table 3). Hematite was frequently accompanied by anhydrite, which probably forms from reactions between pyrite sulphur and calcite. According to literature review anhydrite and hematite began to form at 500 °C and were major phases through 800 °C.

Scanning Electron Microscope (SEM)

Morphology, texture and chemistry of the samples were analysed. Examination showed that the fly ash samples are different in comparison with the conventional fly ash. The majority of the quartz crystals remains and appears as angular particles due to the relatively low temperature in the Circulating Fluidised Bed furnace. In general the CFB fly ashes have a subangular form as they contain bi-mineral and multi-mineralogical phases and quartz is mixed with calcium and aluminosilicated phases.

The majority of mineral phases, which were identified by XRD, were also verified by SEM. Some of the most common mineral phases are show in figure 3.

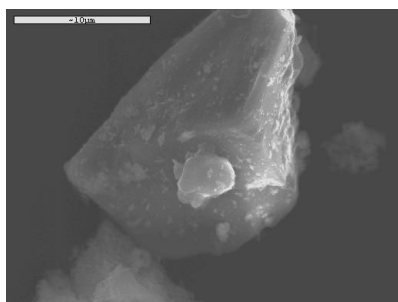


Figure 3a: The mineral quartz in sample C3

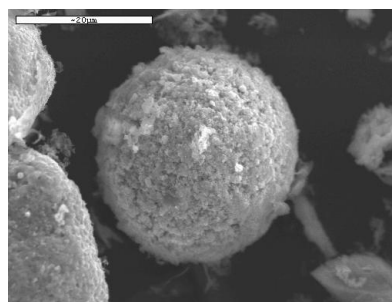


Figure 3b: The mineral hematite in sample C1

Conclusions

Compared to fly ash from combustion of wood chips, the co-combustion ashes studied had lower contents of calcium, potassium and magnesium. The blend of coal and wood chips adds aluminium and iron to the ash and the trace element levels were generally in the same ranges as for wood fly ash. The trace elements which may cause some concern are As and Cr in the case of sample F1 (lignite) and F2 (lignite/wood chips), which in addition are of small particle size. Many of the trace elements in fly ash show a definite concentration trend with decreasing particle size.

Fly ash deriving from the combustion of pure lignite and pure wood chips has a low LOI level. If the SO_3 content is taken additionally into account ($SO_3 < 5\%$), then the most attractive fly ash to the cement industry is C1 (lignite), collected at the second cyclone.

Moreover, the particle size distribution of the examined fly ashes is related to the fuels burned. The higher the percentage of biomass in the blends, the smaller the ash particle size.

The mineralogical composition of the fly ashes depends on the components of the blends and the combustion temperature. The presence of minerals such as anhydrite and portlandite is more possible when the used fuels contain calcium; therefore fly ash derived from wood chips contains the aforementioned minerals. Also, the occurrence of minerals such as sylvite is noticed when the fly ash derives from the combustion of biomass, due to the higher concentration of alkalis in this fuel.

The chemical characteristics of the blend of biomass/coals depend on the system of combustion and the fly ash capturing mechanism. That is mainly because the combustion furnace type and combustion process are closely related to the degree of coal combustion, combustion temperature, and combustion efficiency.

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