

Utilisation of Biomass Co-combustion Residues Coming from Pulverised Coal Boilers

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ABSTRACT

The effect of biomass co-combustion with coal on ash quality and utilization aspects was investigated. Co-combustion tests were performed in lab, semi-industrial and industrial scale plants, using several coal-biomass blends. Two different sets of co-combustion residues were analysed according to their production process and analysis method. Samples collected from lab and semi-industrial scale tests were analysed for major elements and heavy metals content, loss on ignition (LOI), free CaO content and their grain size distribution. Natural radioactivity and radon exhalation rate were also measured in samples collected from tests performed at large-scale power plants. The effect of biomass co-combustion on the radioactivity content of fly ash was dependent on the fuel mixture used as well as the ash sampling location along the flue gas pathway. The results showed that properties of co-combustion residues are directly connected to the combustion conditions and individual blend components. Biomass utilisation as secondary fuel in co-combustion processes is technically and economically feasible up to 20% ^{w/w} and the produced ash could be further utilised without any major treatment.

KEYWORDS: Co-combustion ash, analyses, heavy metals, radioactivity.

INTRODUCTION

Disposal of ash coming from coal-fired power stations has caused significant economic and environmental problems. Several alternative uses of coal ash as a value-added product beyond its incorporation in construction materials were developed or are still under investigation, aiming to reduce ash disposal and its negative effects. Namely, fly ash is mostly used in the cement and concrete industry, while further applications for building materials, road works, binders, gypsum wallboards, mineral wool production, lightweight ceramics, metallurgy, waste water management, landfilling and agriculture have been reported¹⁻¹⁴. The uses of fly ash define the significant parameters, i.e. physical, chemical and mineralogical properties, which should be

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determined. The related characterisation methods are mainly included in the standards governing the utilisation of fly ash.

Apart from national legislation, EN 450 “Fly ash for concrete” regulates the minimum requirements on fly ash, which is used as a component of concrete in many European countries. EN 450 Standard refers to ashes from coal combustion and within its revision residues from biomass and coal co-combustion will be also included. In this way, fly ash will be defined as a fine powder of mainly spherical, glassy particles, derived from burning of pulverised coal, with or without co-combustion materials. Possible co-combustion materials are vegetable material like wood chips, straw, olive shells and other vegetable fibres, green wood and cultivated biomass, animal meal, municipal sewage sludge, paper sludge, petroleum coke and virtual ash free liquid and gaseous fuels. The fly ash from co-combustion should be obtained from a mixture of pulverised coal and co-combustion materials, where the minimum percentage, by dry mass, of coal is greater than 80 % and where the maximum proportion of ash derived from co-combustion material does not exceed 10 %. It is expected that this revision in EN450 will seriously influence the European situation of fly ash utilisation.

The aim of this paper is to present the properties of different co-combustion residues with respect to their potential uses and legislative restrictions. The ash samples of several coal/biomass blends were produced in lab-scale, pilot-scale and industrial facilities and were subject to ash characterisation methods and radioactivity measurements. Specifications concerning the composition of co-combustion residues were accrued based on the analysis results. Since a variety of co-combustion ashes were investigated, it is expected that the indications provided to the potential users of this type of residues will be proved valuable for future applications.

METHODOLOGY

Fuel blends formation and ash production

Two different sets of co-combustion residues were analysed according to their production process and analysis method. In the first series, biomass samples, characteristic of the Greek region were used to produce ashes in lab-scale and pilot-scale facilities. The facilities and the fuel test matrix elaborated in the first experimental series are shown in Table 1. Co-combustion residues were initially produced in an electric muffle furnace. An extensive series of experiments were realised in a 0.75 MW_{th} hot water boiler, in which fly and bottom ash samples were collected. Finally, ash samples were collected during the co-combustion experiments at the

Table 1. Facilities and fuel blends used during the first series of co-combustion tests for ash production.

Facility	Coal	Secondary fuel (%wt)	Secondary fuel share (%wt)
Lab-scale (muffle furnace)	Ptolemais lignite	Forest residue Olive kernel	5, 10 & 20
Hot water boiler, 0.75 MW _{th}	Ptolemais lignite	Forest residue Olive kernel	approx. 20
CFBC, 1 MW _{th}	Ptolemais lignite (xylic type)	Demolition wood Railway sleepers	25

1MWth CFBC unit in Vienna, Austria. Greek lignite was the main component of the fuel blend and ash samples were collected and analysed for their major elements.

The second series of co-combustion ashes were produced in one pilot facility in Germany (IVD, University of Stuttgart) and several large-scale power plants in Sweden (Vattenfall, VU) and Denmark (ELSAM). Nine different fuel blends were tested at IVD's installation and ash was sampled at five points in each test case. Namely, bottom ash was sampled at the hopper and fly ash was collected directly from the combustion chamber, the air preheater, the cyclone and the filter. Details on the examined fuel blends are presented in Table 2. Vattenfall provided fly ash samples from five Swedish plants – four pulverised fuel boilers (in Helsingborg, Västerås, Uppsala (Fyris), and Jordbro) and one fluidised bed boiler (in Nyköping (Idbäcken)) - as shown in Table 3. Five fly ash samples were collected when co-firing straw at ELSAM's power plant on 30/1/2003 and weeks 9, 10, 11 and 12 of 2003, respectively. Most of these ash samples were tested for their natural radioactivity content and radon exhalation rate analysis.

Table 2. Codes and fuel blends of the IVD ash sample sets.

Code	Primary Fuel	Secondary Fuel
GB100	Götelborn hard coal 100%	-
GB/H1 53/47	Götelborn hard coal 53%	Wood 47% (from Vattenfall)
GB/H1 80/20	Götelborn hard coal 80%	Wood 20% (from Vattenfall)
GB/H2 66/34	Götelborn hard coal 66%	Wood - Helsingborg 34% (from Vattenfall)
GB/H2 80/20	Götelborn hard coal 80%	Wood - Helsingborg 20% (from Vattenfall)
GS 95/5	Götelborn hard coal 95%	Straw 5%
GS 86/14	Götelborn hard coal 86%	Straw 14%
CoS 83/17	Columbian hard coal 83% (COCER, from Techwise)	Straw 17%
P18A	Götelborn hard coal 82%	Poplar wood 18%

Fuels and ash characterisation

ASTM methods were applied for the determination of primary properties of the solid materials. Typical analyses of the fuels are given in Table 4. Characterisation of ash samples coming from the first series of co-combustion experiments was carried out aiming to investigate the potential of co-combustion residues utilisation in construction works. Sulphur trioxide, moisture, carbon content (Loss On Ignition), total oxides, magnesium oxide, morphology, pozzolanic activity and fineness are the most important characteristics to be examined during the fly ash utilisation in the cement and concrete production process. An ICP-AES spectrophotometer was used for the analysis of heavy metals, since some of them are of environmental concern. The determination of the major elements and heavy metals was carried out both for the raw material and the ash samples. Furthermore, the Loss on Ignition (LOI), the Free CaO content and the grain size distribution were measured in each collected ash sample.

Table 3. Codes and fuel blends of the Vattenfall fly ash samples.

Code	Power Plant	Fuel
Fyr14	Fyris, Uppsala	70 % Swedish peat, 30% wood
Fyr16	Fyris, Uppsala	50% Estonian peat, 50% (70% Swedish peat, 30% wood)
Fyr25	Fyris, Uppsala	100% hard coal
Fyr26	Fyris, Uppsala	60% (70% Swedish, peat 30% wood), 40% Russian peat
Hbg12	Helsingborg	40% Bio, 50% hard coal, 10% TASP
Hbg15	Helsingborg	40% Bio, 50% hard coal, 10% TASP
Idb10	Idbacken, Nykoping	10% hard coal, 22.5% waste wood, 67.5% forest residue
Idb22	Idbacken, Nykoping	17% hard coal, 13% waste wood, 70% forest residue
Jbr10	Jordbro	100% bio fuel (wood)
Vas11	Vasteras	70% hard coal, 30% peat
Vas21	Vasteras	70% hard coal, 30% peat

Table 4. Proximate and ultimate analysis of Greek lignite and secondary raw materials.

	Lignite	Pine wood	Oak wood	Olive kernel
Proximate analysis, % w/w (as received)				
Moisture	53.8	28.20	23.55	13.50
Volatiles	23.24	67.49	66.89	61.10
Fixed carbon	10.58	3.70	8.94	16.70
Ash	12.38	0.61	0.60	8.70
Ultimate analysis, % w/w (dry basis)				
C	43.19	39.58	38.95	40.53
H	4.09	5.17	4.97	4.70
N	1.43	0.08	0.11	2.79
S	1.33	0.19	0.04	0.50
O *	23.16	54.13	55.13	41.38
Ash	26.80	0.85	0.80	10.10

* by subtraction

Radioactivity measurements

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) estimated that electrical energy production using coal leads to a total collective effective dose equivalent commitment of 2 manSv/Gwa¹⁵. Therefore, the radioactivity content of combustion residues should be considered when examining possible utilization scenarios.

Radiation Protection document 112 of the European Commission¹⁶ defines the Radiation Protection Index (RPI) of a building material as:

$$RPI = C_{Ra} / 300 \text{ Bq kg}^{-1} + C_{Th} / 200 \text{ Bq kg}^{-1} + C_K / 3000 \text{ Bq kg}^{-1} \quad (1)$$

where C_{Ra} , C_{Th} and C_K are the ²²⁶Ra, ²³²Th and ⁴⁰K activity concentrations in Bq kg⁻¹. This index is used to identify building materials that may lead to an unacceptable excess dose rate to

building occupants. The RPI has been introduced based on conservative estimates for model buildings, and has been designed to cover both direct gamma exposure as well as exposure to Radon. Since the RPI should be used as a starting point in assessing building materials regarding the radiation protection, the determination of activity concentration of these three nuclides should be considered the minimum requirement when examining ash.

The radioactivity content of the raw fuels, their blends and the produced ashes was examined for the second series of co-combustion experiments. High-resolution high efficiency Ge detectors were used for the γ -spectroscopic determination of natural radioactivity content of fuels and produced ashes. The effect of combustion parameters on radioactive disequilibrium was examined. In addition, radon exhalation rate measurements from fuels and the ashes produced, as well as from building materials with ash additives were performed, using two airtight radon chambers of 1.8 m³ and 8.5 m³ volume, respectively.

RESULTS AND DISCUSSION

Ash characterisation

Main components in fuel ash: Ash chemical analyses of Ptolemais lignite, two wood species and olive kernel are presented in Table 5. The content of CaO in wood ash is higher compared to the lignite ash, exceeding 50 (% w/w) in pine wood. A high content of CaO refers to self-hardening effects of ash and it is attributed to the sample's higher hydraulic reactivity. Additionally, ash samples of wood species show very low SiO₂ content, which is characteristic of low-pozzolan-ashes. In contrast, olive kernel ash is characterised as pozzolan reacting residues, due to its high content of amorphous SiO₂ and low concentration of CaO. As concerns total alkalis, biomass ashes have a much higher content of K₂O, as high as 18.62 (% w/w) in the oak wood ash. A slightly increased Na₂O concentration has been detected in the olive kernel sample in comparison to the lignite and wood ashes.

Table 5. Ash analyses of raw materials (% w/w).

Compound	Lignite	Pine wood	Oak wood	Olive kernel
SiO ₂	32.65	14.45	16.21	45.05
Al ₂ O ₃	17.27	2.71	2.37	6.98
Fe ₂ O ₃	8.74	1.61	0.54	6.24
CaO	21.24	51.3	46.24	22.90
MgO	5.28	8.00	7.11	3.77
SO ₃	6.00	-	-	1.57
Na ₂ O	0.3	0.17	0.24	0.93
K ₂ O	0.8	10.04	18.62	9.18
P ₂ O ₅	0.30	2.82	4.02	2.36
Rest	7.42	8.90	4.64	1.01

Unburnt carbon: Depending on the biomass share in the fuel blend, co-combustion residues may have a completely different composition than the reference case of lignite ash. Aiming to identify such differences in the ash behaviour, co-combustion residues were produced in a muffle furnace and a 0.75 MWth hot water boiler. The results of ash analysis for the laboratory produced samples are shown in Table 6. Ash samples from exclusively biomass combustion

exhibit high levels of unburnt carbon, measured both as loss on ignition or sum of carbon and hydrogen contents. The lowest values of LOI were obtained when both biomass residual types were added in the fuel blend at the same weight ratio. Quite different observations derive from the analyses of the ash samples from the pilot-scale tests. Fly and bottom ash was collected from about 30 tests in the 0.75 MW_{th} hot water boiler. The ones that best illustrate ash properties variations in lignite-biomass blends are presented in Table 7. Unburnt carbon is considerably higher in all test cases, even when lignite is burnt alone. The lowest unburnt carbon values are met when biomass is combusted with small amounts of PVC, indicating the improved combustion conditions in these test cases. Deviations in carbon content and combustibles cannot be explained by blend composition. In contrast, ash characterisation of laboratory produced ash shows that the sample properties can be directly connected to the share of the blend components. Any observed deviations are within the experimental error of acceptable range.

Reactive components: Free CaO content in the fly ash may react with water to form Ca(OH)₂, resulting in increased volume and structural destruction. When using fly ash in concrete applications, free CaO should be less than 1%wt in order to inhibit this reaction. This is valid only for the fly ash samples collected in the pilot-scale experiments during the co-combustion of lignite, PVC and one of the two biomass residuals, i.e. forest residue or olive kernel. The highest free CaO content was measured in the fly ash sample coming from the lignite combustion.

Grain size distribution: In general, the particle morphology depends on the combustion conditions. Pozzolanic properties of fly ash samples are more intensive when the particle diameter is decreased. Distribution of the grain size of ash samples collected during the pilot-scale tests is illustrated in Figure 1. Coarser particles are mainly found in ashes from the co-combustion of lignite with biomass residues. The higher fraction of finer fly ash particles was observed when burning lignite only, indicating its increased specific surface and improved pozzolanic properties.

Trace elements: Total content of trace elements in the co-combustion residues of the pilot-scale tests are shown in Table 8. Higher content of heavy metals was measured in the bottom fly ash of forest residue compared to olive kernel. Ca has the highest concentration in examined samples and this is mostly characteristic in the lignite ash. The metal element content in the fly ash collected from the cyclones and the filter during the co-combustion tests in the CFBC installation is illustrated in Figures 2. The respective results for the bottom ash of the combustion chamber are presented in Figure 3. Lignite has, by far, the highest ash content and thus the majority of the metal elements detected in the ash samples came from the lignite ash. Increased heavy metal concentrations are observed in the fly ash samples, Figures 2, due to the addition of limestone in the bed. The latter increases fine particulate emissions and results in higher metal emissions, such as Mn, Co, Ni, Cr, Pb, Cd, Sn, V and Ti. Low concentrations of the metal elements Co, Ni, Cr, Pb, Cd, Cs and V were measured in the bottom ash samples, Figure 3. The high concentration of Ti is attributed to its low volatility.

Leaching and toxicity behaviour of co-firing ashes: The toxicity of the liquid samples collected by the TCLP leaching test was estimated using the Microtox toxicity test which is based on the reduction in bioluminescence of the marine bacterium *Vibrio Fischeri*.

Table 6. Analyses of ash samples coming from the lab-scale tests.

Analysis	Lignite – Forest residue – Olive kernel Ratio (% w/w)										
	100/0/0	0/100/0	0/0/100	95/5/0	90/10/0	80/20/0	95/0/5	90/0/10	80/0/20	90/5/5	80/10/10
Ultimate analysis, % w/w (dry basis)											
C	0.69	6.61	7.32	0.60	0.88	0.67	0.65	0.76	0.61	0.51	0.55
H	0.27	0.19	0.46	0.20	0.29	0.20	0.27	0.21	0.28	0.14	0.14
N	0.37	2.98	1.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	1.38	0.00	0.00	1.82	1.82	1.87	2.06	1.22	0.73	2.54	2.67
Heating value, kcal/kg (dry basis)											
Gross	185.5	608.5	760.0	163.6	218.4	168.8	197.1	164.2	166.1	155.0	159.8
Net	171.4	598.6	736.1	153.3	203.4	158.8	183.3	153.6	151.6	147.6	152.6
Loss on ignition, % w/w (dry basis)											
LOI	4.40	23.18	16.90	4.15	4.84	4.25	4.20	4.33	4.13	3.29	2.61
Free CaO, % w/w (dry basis)											
CaO	4.84	2.79	3.25	1.32	1.64	2.09	3.11	3.19	2.31	2.88	2.28

Table 7. Analyses of ash samples produced in the pilot-scale tests at the 0.75 MW_{th} hot water boiler.

Analysis	Lignite – Forest residue – Olive kernel Ratio (% w/w)									
	Test I	Test II	Test III	Test IV	Test V	Test VI	Test VII	Test VIII	Test IX	Test X
	0/0/97*	0/97/0*	78/0/19*	78/0/19*	78/19/0*	78/19/0*	0/0/100	0/0/100	100/0/0	100/0/0
	<i>Bottom</i>	<i>Bottom</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>
Ultimate analysis, % w/w (dry basis)										
C	1.14	1.14	14.17	25.58	16.99	28.1	3.67	16.67	13.52	14.18
H	0.07	0.11	1.02	0.58	1.51	1.95	0.37	2.81	0.37	0.57
N	0.00	0.43	0.58	0.73	0.33	0.41	2.18	2.14	0.42	0.30
S	0.00	0.00	0.00	0.00	0.00	0.00	0.15	1.22	0.16	0.21
Heating value, kcal/kg (dry basis)										
Gross	116.7	131.3	1,511.4	2,297.5	1,909.3	2,461.6	431.6	2,362.4	1,237.7	1,363.7
Net	113.3	125.7	1,459.2	2,267.7	1,832.5	2,361.2	412.6	2,218.4	1,218.9	1,334.4
Loss on ignition, % w/w (dry basis)										
LOI	6.19	6.47	22.02	28.78	15.68	22.24	22.11	36.79	39.68	28.04
Free CaO, % w/w (dry basis)										
CaO	2.95	1.51	1.21	0.54	5.38	0.66	2.72	1.03	1.06	10.33
Water soluble alkalis, % w/w (dry basis)										
Na	0.47	0.56	0.11	0.13	0.36	0.06	0.06	0.10	0.12	0.06
K	5.89	9.25	1.16	1.08	7.95	0.83	0.59	0.75	0.92	0.36

Table 8. Trace elements concentration (ppm) in the ash samples produced in the pilot-scale tests at the 0.75 MW_{th} hot water boiler.

Element (ppm in ash)	Lignite – Forest residue – Olive kernel Ratio (% w/w)									
	Test I	Test II	Test III	Test IV	Test V	Test VI	Test VII	Test VIII	Test IX	Test X
	0/0/97*	0/97/0*	78/0/19*	78/0/19*	78/19/0*	78/19/0*	0/0/100	0/0/100	100/0/0	100/0/0
	<i>Bottom</i>	<i>Bottom</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>	<i>Bottom</i>	<i>Fly</i>
Zn	160±20	345±50	125±20	330±150	315±30	120±10	220±10	1030±30	210±20	210±20
Cu	185±10	135±10	63±5	47±2	37±2	65±5	210±10	400±20	45±5	45±5
Co	21±2	20±2	32±2	36.5±2	30±2	29±2	22±2	19±2	30±2	30±2
Cd	<10	27±1	11.5±1	<10	10.7±2	26±2	<10	<10	<10	<10
Ni	295±20	200±20	440±50	510±40	435±30	380±30	525±30	290±15	490±20	490±20
Mn	1065±100	3750±250	410±20	470±30	665±30	1365±70	560±40	1850±70	230±30	230±30
Cr	225±20	200±20	320±30	450±30	320±30	290±30	597±40	320±10	400±30	400±30
V	47±5	45±5	175±10	190±20	180±10	150±10	40±3	45±3	175±10	175±10
Ti	1340±70	4400±300	2540±200	1910±100	2140±150	2075±100	1020±40	530±30	2175±100	2175±100
Fe (%)	3.4±0.3	9.3±0.5	5.2±0.5	4.7±0.1	6.6±0.2	11.3±0.8	2.5±0.2	2.4±0.08	4.5±0.2	4.5±0.2
Mg (%)	3.6±0.1	2.4±0.1	3.2±0.2	3.4±0.2	3.0±0.1	2.5±0.2	3.1±0.2	2±0.05	2.9±0.1	2.9±0.1
Ca (%)	16.8±1	14.7±1	21±1	24.4±0.9	22±0.4	21.4±0.8	13.7±0.6	9.7±0.4	22±1	22±1
Al (%)	2.5±0.2	1.8±0.2	6.4±0.4	5.3±0.3	5.5±0.2	3.9±0.2	1.6±0.1	1.8±0.03	5.7±0.2	5.7±0.2
Ag	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75
As	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75
Pb	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75
Sn	<75	<75	<75	<75	<75	<75	<75	<75	<75	<75
Na	7400±600	7600±600	4500±600	4430±400	4200±400	6280±700	4770±200	7950±500	2685±100	2685±100

* Samples also contain 3% w/w PVC

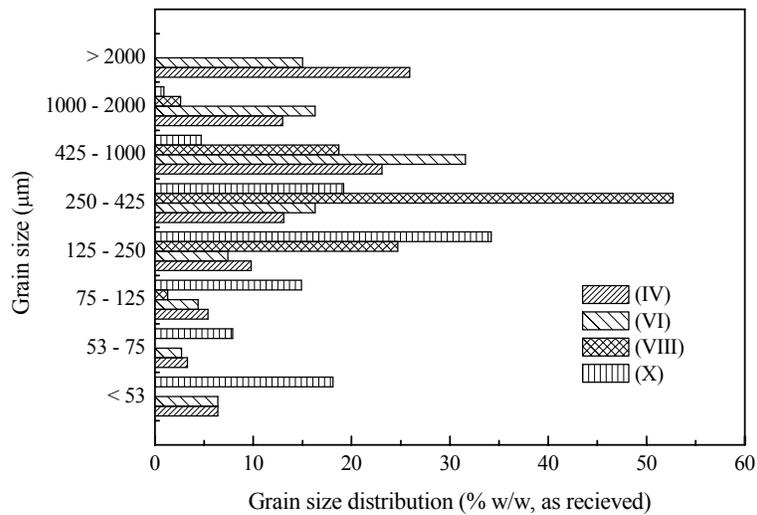


Figure 1. Grain size distribution of fly ash samples collected during the pilot-scale co-combustion tests.

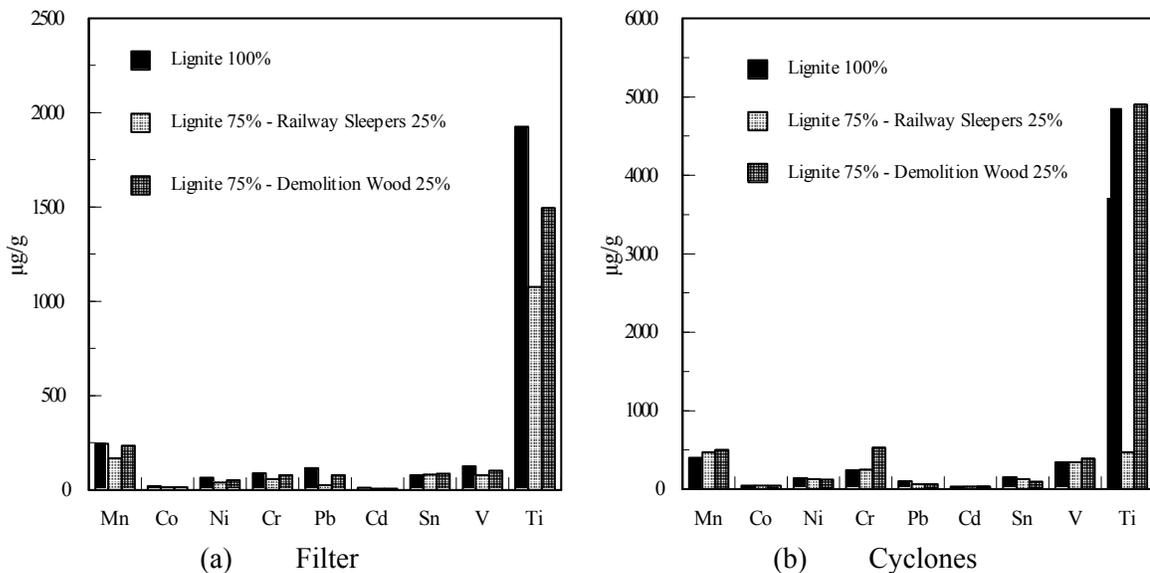


Figure 2. Metal element concentrations in the fly ash (a) filter, (b) cyclones of the CFBC samples.

The pH values of the liquid samples were adjusted at 7 ± 0.2 before the tests in order to ensure that the toxicity is only due to the substances that are present in the samples and not to the effect of pH on the test bacteria. High concentrations of Ca, K and Na were detected in most TCLP liquid samples, while Ag, Cu, Pb, Se, Sn were not extracted to aquatic phase in most cases. The release of contaminants from the solid samples to the liquid phase might be influenced by several physicochemical factors such as the type of the leaching medium, the particle size, the pH, the complexing agents that may be present in the solid sample and various reaction kinetics¹⁷⁻¹⁸.

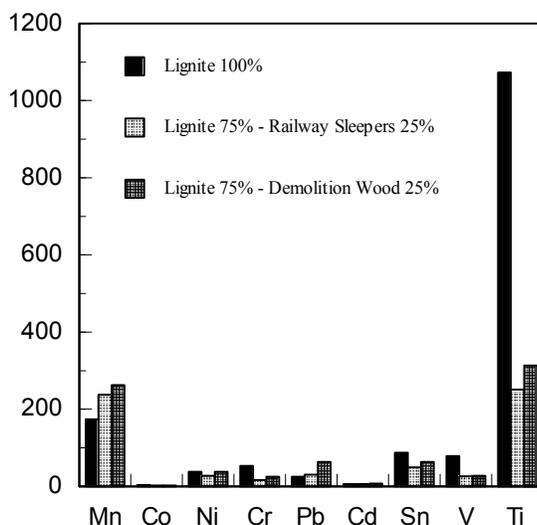


Figure 3. Metal element concentrations in the bottom ash of the CFBC samples.

The results obtained by measuring the toxic effects of the TCLP leachates on *Vibrio Fischeri* within exposure times 5, 15, 30 min, following the 45% and 82% Screening test protocols, with pH adjusted at $7 \pm 0,2$ are illustrated in Figures 2 and 3, respectively. The toxic effect of the most leachates on *V. Fischeri* is significantly low for the 45% Screening test, while the toxicity measured by the 82% Screening test protocol is relatively high, up to 46%. However, the liquid sample VIII (olive kernel) caused the highest toxic effect in both protocols, which could be attributed to the precipitation that was observed during the pH adjustment. The chemical analysis of the leachates showed that the concentrations of Zn, Ni, Mn, Co, Cd were relatively high for the liquid sample VIII. Thus, it can be assumed that the high toxic effect of the sample VIII on *V. Fischeri* was due to the presence of those metals.

Radioactivity measurements

The results of activity concentration in the fuel samples are presented in Table 9. Uncertainty values of all radioactivity measurements are given as combined uncertainty at the 3σ level. The radioactivity content of most nuclides is generally low, both when compared to coal worldwide typical values of 10-25 Bq kg⁻¹ for the ²³⁸U series and ²³²Th series¹⁵, as well as when compared to Greek lignite, in which samples with ²²⁶Ra and ²³⁸U activities in excess of 300 Bq kg⁻¹ have been reported¹⁹. Analysis of ²³⁸U and ²¹⁰Pb was carried out in one of the fuel samples only; both nuclides were found to be in equilibrium with ²²⁶Ra.

Table 9. Natural radioactivity (²²⁶Ra, ²³²Th, ⁴⁰K) content of the ELSAM fly ash samples.

Sampling Date	Activity Concentration (Bq kg ⁻¹)		
	²²⁶ Ra	²³² Th	⁴⁰ K
30/1/2003	158 ± 8.8	162 ± 9.3	430 ± 28
Week 09/2003	75 ± 4.1	58 ± 3.3	710 ± 39
Week 10/2003	134 ± 7.4	117 ± 7.7	600 ± 38
Week 11/2003	88 ± 4.9	64 ± 3.8	790 ± 44
Week 12/2003	98 ± 5.6	85 ± 5.2	610 ± 36

The results of the activity concentration of ^{226}Ra , ^{232}Th and ^{40}K nuclides, determined for the entire ash sample set are presented in Tables 10-11. The radioactivity levels found are generally comparable to typical values for coal ash¹⁵. However, relatively increased concentration of ^{40}K was detected in many of the samples.

The results obtained from the weekly composite samples collected at the ELSAM power plant show some variability, Table 11, despite that the same fuel blend was used during the entire time period. This may be attributed to the variation in the incoming coal activity content, which may often be encountered even in a single coal deposit, as well as the plant operating conditions and should be taken into account when planning sampling campaigns at large-scale facilities.

With reference case the 100% coal combustion it arises that the introduction of biomass influences the ^{226}Ra and ^{232}Th activity concentration profile along the flue gas pathway, Figures 4 and 5. In particular, an increase in concentration is consistently detected in all Filter and some

Table 10. Cesium-137 activity concentration detected in the VU fly ash samples.

Sample Source	Sample	^{137}Cs Activity Concentration (Bq kg^{-1})
<i>VU</i>	Fyr14	143 ± 8.3
	Fyr16	83 ± 4.7
	Fyr25	1.5 ± 0.46
	Fyr26	79 ± 4.9
	Hbg12	95 ± 6.0
	Hbg15	68 ± 4.3
	Idb10	360 ± 20
	Idb22	190 ± 11
	Jbr10	2400 ± 130
	Vas11	36 ± 3.9
	Vas21	89 ± 5.6

Table 11. Radon exhalation rate measurement results.

Sample Source	Sample	^{222}Rn Exhalation Rate ($\mu\text{Bq kg}^{-1} \text{s}^{-1}$)
<i>Vattenfall</i>	Fyr14	7 ± 1.3
	Fy25	42 ± 1.5
	Fyr26	17 ± 3.2
	Hbg15	32 ± 3.1
	Idb22	13 ± 4.6
	Vas11	9 ± 1.6
	Vas21	31 ± 1.2
	Jbr10	20 ± 16
<i>ELSAM</i>	30/1/2003	26 ± 0.94
	Week 09/2003	5 ± 1.2
	Week 10/2003	5 ± 1.1

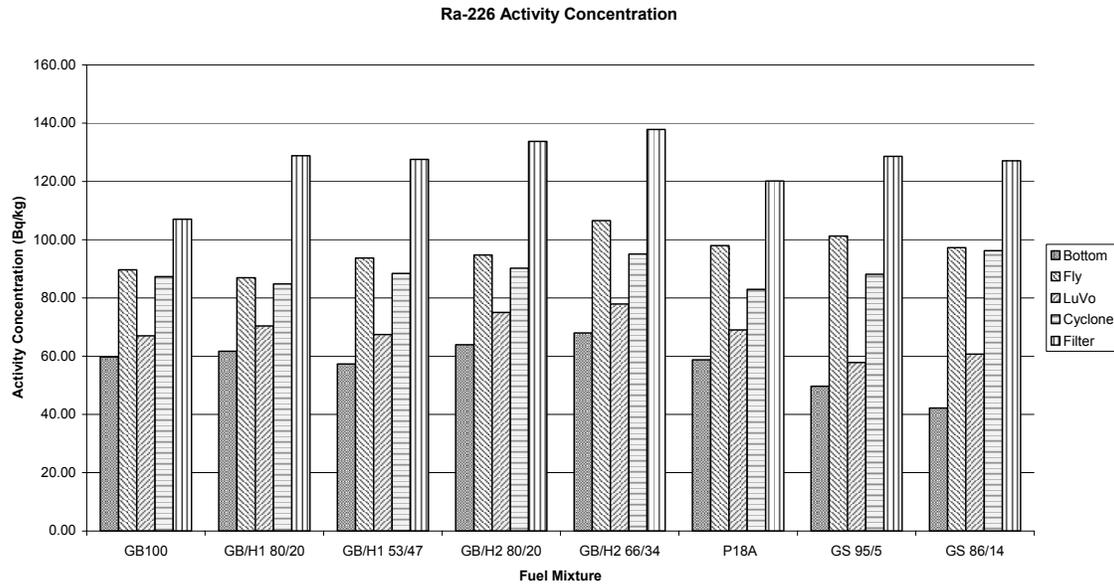


Figure 4. Ra-226 activity concentrations for the IVD sample set.

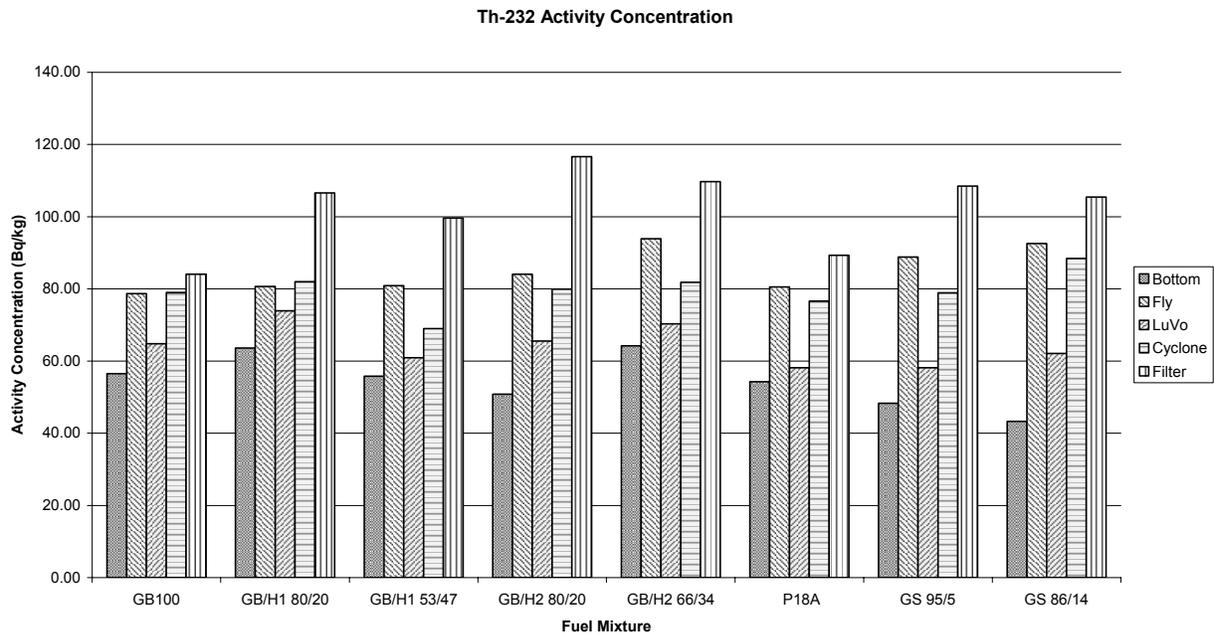


Figure 5. Th-232 activity concentrations for the IVD sample set.

Cyclone fractions, when the biomass share is enhanced. Furthermore, a decrease in activity is observed in the Air Preheater and Bottom Ash fractions produced when straw is used as substitute fuel. The activity concentration of ^{40}K generally increases as the biomass share increases, presumably due to the high concentration of ^{40}K in biomass, Figure 6. The artificial radionuclide ^{137}Cs was detected in some of the fly ash samples; activity concentration values for these samples are presented in Table 12. Similar observations have already been reported in the literature^{20, 21}.

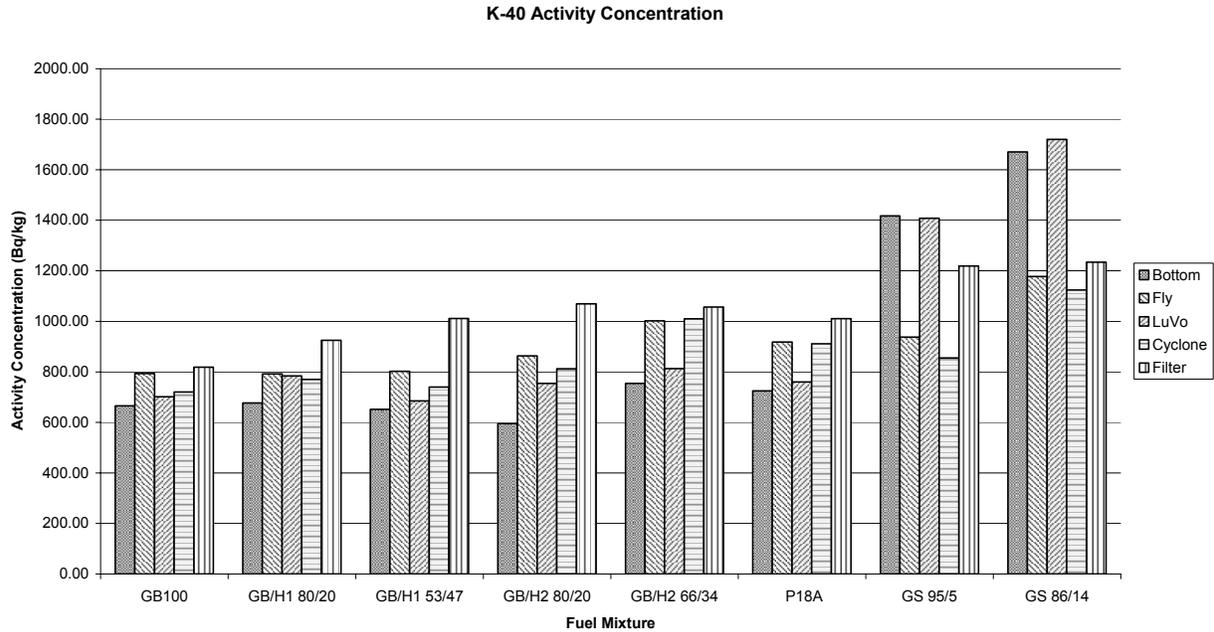


Figure 6. K-40 activity concentrations for the IVD sample set.

Table 12. Cesium-137 activity concentration detected in the VU fly ash samples.

Sample Source	Sample	¹³⁷ Cs Activity Concentration (Bq kg ⁻¹)
<i>VU</i>	Fyr14	143 ± 8.3
	Fyr16	83 ± 4.7
	Fyr25	1.5 ± 0.46
	Fyr26	79 ± 4.9
	Hbg12	95 ± 6.0
	Hbg15	68 ± 4.3
	Idb10	360 ± 20
	Idb22	190 ± 11
	Jbr10	2400 ± 130
	Vas11	36 ± 3.9
	Vas21	89 ± 5.6

Results of the radon exhalation measurements performed are presented in Table 13. The exhalation rate values reported are in general within expected reference ranges. In comparison, Greek fly ash samples have given exhalation rates ranging from 18 – 120 $\mu\text{Bq kg}^{-1} \text{s}^{-1}$ ¹⁹. In addition, ²¹⁰Pb and ²³⁸U activity concentrations were determined for some of the samples. The results of these analyses are presented in Table 14, in comparison to the ²²⁶Ra activity concentration of the samples. For the IVD sample set, the activity concentration of ²³⁸U and ²¹⁰Pb in the Filter fractions is increased in the presence of biomass. Both of these nuclides were found in equilibrium with ²²⁶Ra in coal. Equilibrium between ²³⁸U and ²²⁶Ra in the fly ash seems to have been preserved in most cases, except for the case of the Filter samples in the presence of biomass, where disequilibrium in favor of ²³⁸U is observed. Equilibrium between ²²⁶Ra and ²¹⁰Pb

Table 13. Radon exhalation rate measurement results.

Sample Source	Sample	²²² Rn Exhalation Rate ($\mu\text{Bq kg}^{-1} \text{s}^{-1}$)
<i>Vattenfall</i>	Fyr14	7 ± 1.3
	Fy25	42 ± 1.5
	Fyr26	17 ± 3.2
	Hbg15	32 ± 3.1
	Idb22	13 ± 4.6
	Vas11	9 ± 1.6
	Vas21	31 ± 1.2
<i>ELSAM</i>	Jbr10	20 ± 16
	30/1/2003	26 ± 0.94
	Week 09/2003	5 ± 1.2
	Week 10/2003	5 ± 1.1

Table 14. Uranium series radionuclide (²³⁸U, ²²⁶Ra, ²¹⁰Pb) activity concentration in the samples from large-scale facilities.

Sample Source	Sample	Activity Concentration (Bq kg^{-1})		
		²³⁸ U (²³⁴ Th)	²²⁶ Ra	²¹⁰ Pb
<i>ELSAM</i>	Fly Ash -30/1/2003	160 ± 30	156 ± 8.9	170 ± 19
	Week 09/2003	100 ± 21	75 ± 4.1	90 ± 19
	Week 10/2003	150 ± 22	134 ± 7.4	170 ± 18
<i>VU</i>	Fly Ash -Fyr14	310 ± 23	82 ± 4.8	150 ± 18
	Fyr25	100 ± 12	100 ± 5.5	90 ± 19
	Fyr26	200 ± 16	55 ± 3.3	170 ± 16
	Idb10	40 ± 12	140 ± 20	430 ± 49
	Vas11	180 ± 17	163 ± 9.3	180 ± 19
	Vas21	85 ± 9.9	85 ± 5.1	130 ± 15

was also disturbed in favor of ²¹⁰Pb in many cases. Furthermore, volatile ²¹⁰Pb shows an increasing trend along the flue gas pathway, in a way similar to ¹³⁷Cs. Physical and chemical processes during combustion mainly cause these equilibrium disturbances; similar results for lignite fly ash have already been reported¹⁹.

CONCLUSIONS

Utilisation of fly ash coming from coal-fired boilers brings about significant benefits. The same is valid in case that biomass is used as substitute fuel in the coal-fired boilers. Apart from the cement and concrete industry, co-combustion residues could find different application routes, depending whether the relevant legislative requirements are met. Within the framework of this scope, several blends of coal and biomass were tested in facilities of different scale and the

produced ashes were subjected to various analyses, including major elements and heavy metals determination, loss on ignition (LOI), free CaO content, grain size distribution, natural radioactivity and radon exhalation rate. From the evaluation of all these results, it was concluded that the properties of co-combustion residues are directly connected to the combustion conditions and individual blend components. The radioactivity content and radon exhalation rates of the fuel and ash samples analyzed was found to be generally low, compared to worldwide typical values for coal ash. The activity concentration of the fly ash samples analysed was found to depend on the sampling location along the flue gas pathway as well as the fuel blend used, while radioactive equilibrium in the U series was often disturbed. Biomass utilisation as secondary fuel in co-combustion processes is technically and economically feasible up to 20% ^{w/w} and the produced ash could be further utilised without any major treatment.

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