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GARY URB

Assessment of environmental impact of oil shale fly ash from PF and CFB combustion

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LIST OF ORIGINAL PUBLICATIONS

The present thesis consists of four original research papers and a review.

I. **Urb, G.,** Teinemaa, E., Kirso, U., Kamens, R.M., Tenno, T. (2011). Atmospheric chamber study of oil shale fly ash particles from circulating fluidized bed and pulverized firing processes. (submitted)

II. Laja, M., **Urb, G**., Irha, N., Reinik, J., Kirso, U. (2005). Leaching behavior of ash fractions from oil shale combustion by fluidized bed and pulverized firing processes. Oil Shale, 22, 453–465.

III. Kirso, U., Laja, M., **Urb, G.** (2005). Polycyclic aromatic hydrocarbons (PAH) in ash fractions of oil shale combustion: fluidized bed *vers* pulverized firing. Oil Shale, 22(4), 537–545.

IV. Laja, M., Irha, N., **Urb, G.**, Reinik, J., Kirso, U. (2005). Characterization of water extracts of solid waste generated by oil shale combustion. Proceedings of the Estonian Academy of Sciences. Chemistry, 54(3), 134–141.

Author's contribution

Paper I: Performed all the experimental work and writing the article.

Paper II: Performed and participated in experimental work, calculations, interpretation of results and writing of the article.

Paper III: Performed and participated in experimental work and in writing the article.

Paper IV: Participated in experimental work, calculations and writing the article.

ABBREVIATIONS AND SYMBOLS

BaP	benzo[a]pyrene
CFB	circulating fluidized bed combustion
CHR	chrysene
DBahA	dibenz[a,h]anthracene
ESP	electrostatic precipitator
HPLC	high performance liquid chromatography
ICP-HR-MS	inductive coupled plasma high resolution mass spectrophotometer
LHV	low heating value
PAH	polycyclic aromatic hydrocarbons
PF	pulverized firing
PM	particulate matter
PM 2.5	particles with diameter less than 2.5 μm
PP	power plant
PSD	particle size distribution
STI	Synthesis Toxicity Index
TSP	total suspended particles
US EPA	United States Environmental Protection Agency

1. INTRODUCTION

Any type of fuel combustion is a potential source of pollution. Combustion of oil shale produces a large amount of solid waste and is cause of air pollution. Composition of solid wastes generated by such combustion is dependent of the fuel and combustion technology used.

14.2 million tons of commercial oil shale was combusted in thermo-electric power plants in Estonia in 2010 [1]. Thermo-electric power plants are one of the biggest fossil fuel consumers and pollution sources in the World, including in Estonia [2]. Approximately 75% of pollutants (CO_2, SO_2, NO_x, fly ash) in Estonia are emitted by the Baltic and Estonian Power Plants (PP), which rank among the ten biggest sources of air pollution in Europe [3]. Over 90% of Estonian primary power supply is covered by two oil shale PPs located close to Narva city (together referred to as Narva PPs). Both of these are steam turbine power generation plants.

The main technology of processing the oil shale in the PPs until 2004 was the combustion of pulverized fuel (PF) within boiler type TP 101. At present time a new technology, circulating fluidized bed combustion (CFB) process has been installed. One 200 MW power unit at Baltic PP and one 200 MW power unit at Estonian PP were repowered and upgraded to 215 MW with two CFB boilers in 2004–2005 [4,5]. Today both technologies (PF and CFB) are currently used in Narva PPs. Repowering two new boilers with CFB technology increased the efficiency of electricity production of the aggregates by 2%. The renovation of power units in Narva PPs with installation of more efficient flue gas filters in 2005 led to a remarkable reduction of pollutant emissions into the air (e.g., SO_2, NO_x and solid particulates) [6].

Today the lower heating value (LHV) of oil shale used for electricity production is approximately 8.3–8.5 MJ/kg [7–9]. This is a low-grade fuel with a high content of carbonate minerals compared to coal which has typical value of 25 MJ/kg [10]. Burning of the oil shale is always associated with several technological ja environmental problems related to dissociation of carbonate minerals, high CO_2 emission levels, ash handling and storing and emissions to atmosphere [9].

Processing one ton of oil shale creates up to half a ton of mineral residue, ash, most of which is currently deposited in ash fields. The Baltic and Estonian PP ash fields near Narva are Estonia's largest waste handling locations and cover a total of ca 13 km^2. Narva PPs deposited a total of 7.0 million tons of oil shale fly ash and bottom ash in 2010 [1]. The overall amount of oil shale ash disposed in ash fields is 117 mln T and 123 mln T, from Baltic PP and Eesti PP respectively [11].

To deposit oil shale fly ash and bottom ash, the hydro transport is used. In hydro transport, the fly ash and bottom ash from the power plants are mixed with water and transported as slurry to the processing zone of the ash field, where the solid material is allowed to settle so that the water can then be re-routed back to the transport system through an intermediate pond. This process

changes the chemical properties of the water circulating in the system; the pH of the transport water is as high as 13 due to the hydrolysis of CaO in the oil shale ash into CaOH. The water circulating in the system also contains various chemical compounds and ions (K^+, Na^+, SO_4^{2-}, Cl^-). The ash transport and depositing system is closed, which means that the transport water circulates within it, without escaping into the environment. Changes in production levels and the amount of precipitation mean that excess transport water must sometimes be removed from the system in order to maintain stability. Before the water is released into the environment, it is neutralized to a pH of 9 or less, which is a level that is suitable for natural environments [1]. According to the data, the area of groundwater polluted by oil shale ash leachate was 9 km^2 [12].

According to the initial plans two PF boilers in the Narva PPs are expected to be replaced with 300 MW CFB boilers in 2012 [13], but based on the latest news a new PP on CFB technology, will be constructed close to Narva and first unit will be ready in 2015. As a nuclear PP is not expected to be built in the foreseeable future in Estonia, the output of PPs will not be reduced. [14]

In the context of minimizing the environmental impact of power production from oil shale, the question has arisen about the efficiency of utilization of oil shale. The modern CFB technology at the Narva PPs provides advantages in utilization of upgraded oil shale with the LHV up to 11.0 MJ/kg. Several positive aspects of using the oil shale of higher quality can be highlighted: decreased concentration of CO_2 in flue gas, reduction of fuel consumption per kWh of produced power, and the improvements in ash handling and storing [9].

According to a moderate scenario of Estonian economic growth, it is probable that consumption of oil shale will not decrease in next 15–20 years. It would be reasonable to increase the heat value of oil shale in order to utilize oil shale resources more efficiently and with lesser environmental impact [14].

The main purpose of this work is to compare the solid wastes, e.g. fly ash, discharged by the PF and CFB processes, with a special emphasis of toxic trace metals and hazardous organic compounds, particularly polycyclic aromatic compounds (PAH). In general, the environmental impact of the pollutants is related to their availability for transport and bio-uptake, rather than their total concentrations in the soil or waste material. It is of special interest to find out whether there is a difference in the atmospheric behavior and aging of PF and CFB fly ash.

In order to assess environmental and health effects also the ash leaching characteristics will give important information and should be studied.

2. LITERATURE OVERVIEW

2.1. Estonian oil shale properties

Oil shale is a sedimentary rock containing organic matter, kerogen. The mineral matter of Estonian oil shale contains carbonate and terrigenic components.

Oil shale dry matter consists of three parts: organic, sandy-clay and carbonate part. The chemical and mineralogical composition of all these separate components is relatively constant, irrespective of the deposit location and layer. Elemental composition of the organic matter consists mainly of carbon, hydrogen and oxygen (Table 1). Among others, the organic matter contains also on average 1.8% of organic sulphur. An important characteristic of the organic matter is high chlorine content. The mineral matter of oil shale is in two large groups: sandy-clay part and carbonate matter [4]. The chemical composition of the sandy-clay part contains SiO_2 (60%) and Al_2O_3 (16%), which are the main raw materials of stone. The minerals of the carbonate matter are calcite $CaCO_3$, dolomite $CaMg(CO_3)_2$ and siderite $FeCO_3$ [4].

Table 1. Chemical composition of Estonian oil shale, percent [4]

Organic matter		**Sandy-clay part**		**Carbonate part**	
C	77.5	SiO_2	59.0	CaO	48.0
H	9.7	CaO	0.7	MgO	6.6
O	10.0	Al_2O_3	16.0	FeO	0.2
N	0.3	Fe_2O_3	2.8	CO_2	45.0
S	1.8	TiO_2	0.7		
Cl	0.8	MgO	0.4		
		Na_2O	0.8		
		K_2O	6.3		
		FeS_2	9.3		
		SO_3	0.5		
		H_2O	2.6		
Total	**100.1**	**Total**	**99.1**	**Total**	**99.8**

2.2. Ash from oil shale combustion

The ash formed during the fuel combustion is a substance that consists of particles with different size, density, magnetic, and electrical properties; chemical and mineralogical composition; etc.

During the combustion of oil shale several ash fractions are formed. Depending on the technologies used these fractions include bottom ash, cyclone ash, ash from superheater, ash from electrostatic precipitators (ESP) and fly ash. The latter is emitted into the atmosphere with flue gases, being therefore a special concern to environment. It is remarkable that about 6240 tons of particulate matters were emitted to atmosphere in Narva PPs in 2009, despite the use of renovated ESPs [15].

The ash formation conditions (temperature, surrounding medium, fraction composition, etc.) can be rather different depending on the combustion technology used. In PF boilers, the combustion temperature reaches 1400 to 1500 ^{o}C, and the formation of ash takes only a couple of seconds. In CFB boilers, the combustion temperature is lower (800–850 ^{o}C) [5], the fuel injected into the furnace is mixed with recirculating ash particles. In this situation, a mixture of ashes forms under different conditions within the combustor. Since the temperature and composition of flue gas at different points in the boiler gas passage is not the same, the composition and phase state of ash particles is changing along the duct as well [4].

According to Reinik et al., the physical structure of the PF fly ash is coarse when compared to CFB ash. The surface area (0.5 m^2/g) of PF fly ash from the ESPs is comparatively smaller than of CFB fly ash (6.9 m^2/g) [16].

Compositional and morphological properties of PF and CFB ashes are different. Compared to the CFB fly ash, the fly ash from PF is due to higher combustion temperature characterized by a large proportion of spherical glassy and/or hematite particles with a clump of aggregated particles. Ash particles in CFB ashes, where combustion is performed at lower temperature, only rarely show spherical morphology however, and ash is composed of porous aggregates of irregular particles whose grain size gradually decreases along the ash separation tract. The value of specific surface area of CFB ashes is up to ten times higher than in the case of PF ashes [16–18]. PF ashes are dominated by free lime, whose proportion decreases from the furnace to the last field of ESPs. Ashes from CFB boilers show more complex variations, and on several occasions different phases change contrary to PF ashes [17].

From an environmental point of view there are numerous studies available, which describe the properties and environmental behavior of fly ash emitted from PF combustion process [19–21], though less investigations are carried out regarding the behavior and properties of CFB combustion fly ash. The potential hazard of solid particles present in inhaled air depends on particle size and number concentration [22]. Parve et al., have described that the size distribution of solid particulate emissions is dependent on fuel type (Table 2) [23].

Table 2. Size distribution of solid particulate emissions at different fuels firing mass %. [23].

Solid fuel	Particle size fraction		
	<2.5 μm	2.5–10 μm	>10 μm
Coal	13	39	48
Derived coal	30	40	30
Biomass	93	3	4
Waste	60	30	10
Oil shale (PF)	30–59	40–50	5–20
Oil shale (CFB)	55–65	33–43	2–4

The trends of particle size distribution and particulate matter (PM) concentrations at the inlet and outlet of ESP show that electrostatic precipitators clean efficiently flue gases from larger fly ash particles. ESP efficiency at cleaning flue gas flow from particles of the size >10 μm is 63 times higher than from particles <2.5 μm (PM 2.5) [23]. Parve et al., have also described that the concentration from the ESP outlet, particles with a diameter less than 2.5 μm, is 21.3 mg/m^3, particles with a diameter 2.5–10 μm it is 17.1 mg/m^3 and for particles larger than 10 μm is 1.3 mg/m^3, resulting in a total of 39.7 mg/m^3 [23].

Comparison of size distribution of TSP emissions from PF (boiler type TP-101) and CFB boilers reveal that the mass share of fine particles PM 2.5 is about 10% higher in the case of CFB boiler [19]. This could be explained with very efficient milling effect of relatively soft minerals of oil shale at CFB furnace [24].

PM 2.5 particles are likely to penetrate deep into the alveolar sacks of the lung. These particles can accumulate in the respiratory system and are associated with numerous negative health effects. A number of studies have shown that exposure to fine particulate matter is most closely associated with increased hospital admissions and emergency room visits for heart and lung diseases [25]. The PM 2.5 has been connected to an increase in cardiovascular mortality and a number of premature deaths in Estonia [26]. In Narva city the decrease in life expectancy due to PM 2.5 was 0.5 years by earlier study [27].

Recent studies have shown that the toxicity level of heavy metals in oil shale fly ash was significantly enhanced after CFB combustion [28].

It is also known that fine particles emitted from PPs are not only a local issue as they are prone to long range transport and therefore cause a threat to the surrounding environment and its inhabitants.

2.3. Long-range transport of fly ash

The long-range transport of fine particles are investigated and monitored in several studies [29, 30]. In addition, long-range transport assessment of organic pollutants has been studied [31].

The Baltic PP, 5 km southwest of Narva, has been in operation since 1966. The gross capacity today is 765MW per hour and the stack height is 160 m. The

Estonian PP, 20 km southwest of Narva, was connected to the grid in 1973. The gross capacity today is 1615MW per hour and the stack height is 250 m [32, 33]. The emitted particulate matter from these high stacks is prone to long-range transport. Many studies of Estonian soil have shown that the highest concentrations of total PAHs where found in northeastern part of Estonia [34]. Also elevated atmospheric aerosol concentrations are observed approximately 140 km north of the Narva PPs [35].

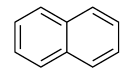
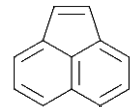
2.4. Ultrafine fly ash particles

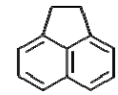
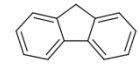
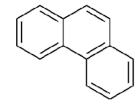
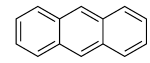
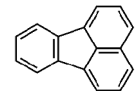
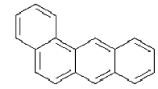
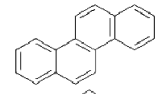
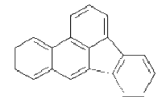
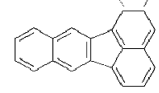
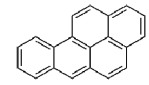
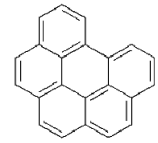
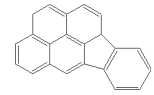
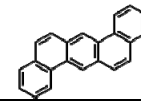
Ultrafine fly ash particles, with diameters less than 0.5 μm, typically comprise less than 1% of the total fly ash mass [36]. These particles are formed primarily through ash vaporization, nucleation, and coagulation/condensation mechanisms, which leads to compositions notably different compared to other fine or coarse particle fractions formed by fragmentation. Earlier studies based on instillation of size segregated fly ash particles in mice, showed that ash aerosols from the ultrafine mode were more toxic than those from either the fine or coarse fragmentation modes [37]. Experiments with coal combustion fly ash have shown that the composition of the ultrafine fraction is significantly different than those of the coarse and fine fractions. Higher concentrations of hazardous and volatile elements occur in the ultrafine fractions than in the coarse or fine fractions, with enrichments of up to 50 times observed for some elements [36]. Possible reasons include enhanced free radical activity and greater surface area [36].

2.5. PAHs

Polycyclic aromatic hydrocarbons (PAHs) are toxic high molecular weight compounds consisting of carbon and hydrogen. Many of these are carcinogenic, mutagenic, and teratogenic. PAH is a class of structurally similar chemical compounds characterized by the presence of fused aromatic rings (Table 3).

Table 3. Characterization of Priority PAH Included in US EPA List [34]

PAH	Abb-reviation	Formula	MW	Mp, °C	Bp, °C	Vapor pressure, Pa
Naphthalene $C_{10}H_8$	NA		128	80	218	1.0×10^{2}
Acenaphthylene $C_{12}H_8$	ACL		152	93	270	9.0×10^{-1}

PAH	Abb-reviation	Formula	MW	Mp, °C	Bp, °C	Vapor pressure, Pa
Acenaphthene **C**$_{12}H_{10}$	AC		154	95	279	3.0×10^{-1}
Fluorene $C_{13}H_{10}$	FL		166	116	295	9.0×10^{-2}
Phenanthrene $C_{14}H_{10}$	PHE		178	101	340	2.0×10^{-2}
Anthracene $C_{14}H_{10}$	AN		178	218	342	1.0×10^{-3}
Fluoranthene $C_{16}H_{10}$	FA		202	111	375	1.2×10^{-3}
Pyrene $C_{16}H_{10}$	PY		202	156	393	6.0×10^{-4}
Benz[a]anthracene $C_{18}H_{12}$	BaA		228	162	435	2.8×10^{-5}
Chrysene $C_{18}H_{12}$	CHR		228	255	448	5.7×10^{-7}
Benzo[b]fluoranthene $C_{20}H_{12}$	BbF		252	168		
Benzo[k]fluoranthene $C_{20}H_{12}$	BkF		252	217	480	5.2×10^{-8}
Benzo[a]pyrene $C_{20}H_{12}$	BaP		252	179	360	7.0×10^{-7}
Benzo[ghi]perylene $C_{22}H_{12}$	BghiP		276	277	550	1.4×10^{-8}
Indeno[1,2,3-cd] pyrene $C_{22}H_{12}$	IP		276	163	530	1.3×10^{-8}
Dibenz[a,h]anthracene $C_{22}H_{14}$	DBahA		278	266		3.7×10^{-10}

PAHs are lipophilic, meaning they mix more easily with oil than with water. The larger compounds are less water-soluble and less volatile. Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or in air. However, they are also a component of concern in particulate matter suspended in air.

It should be noted that, while PAH are often discussed as a group, the individual homologues are evaluated as separate chemicals in the risk characterization [38–41]. There are over 100 chemicals in the family of PAH compounds, although a smaller number are routinely reported at disposal sites.

The United States Environmental Protection Agency (US EPA) has fixed 16 PAH as priority pollutants (see Table 3), effective from 1997 [42, 43]. This set is commonly used globally for hazard identification.

It is well known that the discharge of harmful organic compounds such as various PAH by combustion of fossil fuels is significant [44–47]. As in any fuel combustion, PAH formation and emission mechanisms could be classified in two processes [46, 47]: pyrolysis and pyrosynthesis [44]. On heating, the organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments, mainly highly reactive free radicals with a very short average lifetime, lead to more stable PAH formation through recombination (pyrosynthesis).

The total content of PAH compounds in coal fly ash has been found in the range of 20–290 μg/kg [44, 48], whereas in oil shale ash from PF process it was significantly higher, e.g., 53–505 μg/kg [19, 20, 49]. Reduced operating temperatures in CFB process, have however prompted some concern over possible increased emissions of PAHs.

2.6. Leaching of ash

In general, the environmental impact of the pollutants is related to their availability for transport and bio-uptake, rather than their total concentrations in the soil or waste material. The use of a relatively simple extraction procedure, separation of phases and chemical analysis of the water extract, could help in predicting the fate of a pollutant in the environment [50]. Environmental hazard identification could be made, based on the quantitative estimation of leaching of the contaminants from the solid phase into solution. There are a number of parameters that influence the leaching behavior of a solid material. Therefore the composition of extracts is highly dependent on the test conditions. The effect of pH is dominating because it has the major influence on chemical species, especially carbonates [50]. The cation-exchange capacity and iron/aluminum oxide contents are also important factors, which determine the fate of pollutants in terrestrial environment or waste disposal [51]. Potentially toxic elements leached from fly ash can contaminate soil, groundwater and surface water [51, 52].

To predict the environmental impact of ash disposal systems of oil shale combustion in Narva PPs, it is important to learn which compounds could be released to the environment and to understand the processes involved. Based on this information it is possible to characterize the hazard of waste in site-specific conditions, transport and long-term changes in the utilization/disposal conditions.

2.7. Trace metals and their mobility

Solid fuels contain also trace elements, including heavy metals. Some of the trace elements and their compounds in fly ash are toxic to humans. The release of trace metals takes place during combustion in the furnace and also in the gas passes after exit from the furnace. Some of the more volatile trace elements can pass through ash filters as aerosols and can be carried to the atmosphere along with the flue gas [4]. Information of toxic metals and their mobility, for environmental remediation and waste management, is necessary.

Trace metal emission from coal fly ash have been described by many authors [10, 53, 54]. The volatility of trace elements increased from a larger particle size to a smaller particle size [55]. The surface chemistry of leaching coal fly ash has been studied in an number of countries [55–57]. Koukouzas et al., has specially characterized heavy metals from CFB-derived coal fly ash [56]. Jegadeesan et al., has described that even though the trace metals are present in a relatively small fraction, their cumulative build-up and possible release into neighboring environmental milieu (soils, surface and groundwater) may impact their suitability for beneficial reuse [57]. Also leaching/metal extraction tests have shown that metal release from coal fly ash under natural conditions is not an environmental concern [58–60].

Trace metals from Estonian oil shale and fly ash from PF technology have been studied by Aunela-Tapola et al. The trace metal contents of Estonian oil shale were found to be of the same level as the reported average trace metal contents found in coal [61]. The content and behavior of toxic trace metals (Cd, Hg, Pb, V, Cr, Mn, Co, Ni, Cu, Zn) of oil shale ash in water extraction has been investigated by Kirso et al., [62]. The negligible release (0.1% or less from the initial content) was found for V, Mn, Zn, Pb, Ni, and Co. Cu (0.5–1.0%), Cr and Cd (2.5–3.1%) were the metals of medium mobility [62, 63].

Nevertheless, the release of toxic metals from the ash disposals could be a problem in terms of water and soil pollution.

3. EXPERIMENTAL

3.1. Sample collection

Ash samples for analysis and leaching tests were taken from the major ash collection points from furnace to last unit of ESP (Fig. 1) [9], at unit No. 5 (PF technology) and unit No.8 (CFB technology) from Estonian PP in 2004. For the purposes of a chamber study, fresh ash samples were taken from the last ESP prior the experiment again in 2008 and 2010. Both combustors were operating in steady state during the sampling episodes. The sampling from both units was performed on the same day by specialists of Estonian PP. The process characteristics have been checked and found to be representative. The samples for leaching and chemical analysis were transported to the laboratory the next day after sampling and stored hermetically at cold conditions (4 ^{o}C) until analysis.

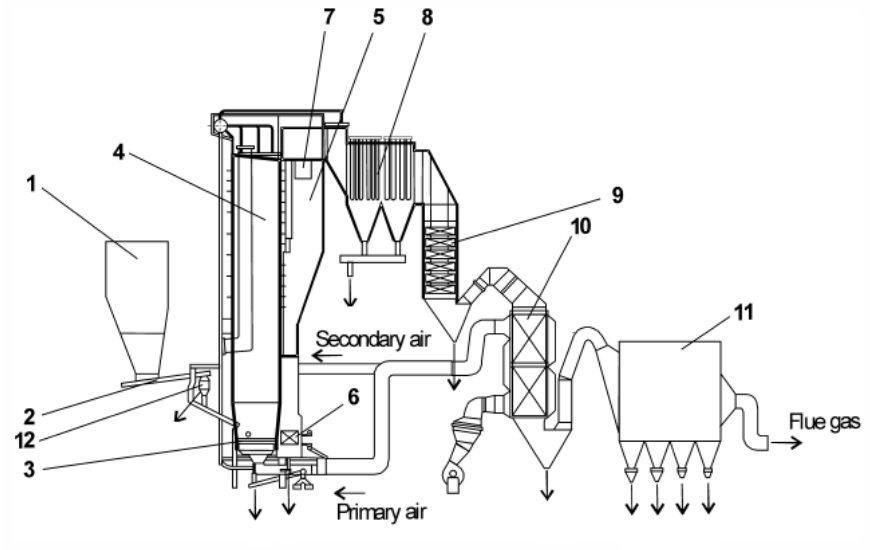


Figure 1. Oil shale-fired CFB boiler [9].
1 – raw fuel silo, 2 – fuel feeder, 3 – grate, 4 – furnace chamber, 5 – separating chamber, 6 – fluidized bed internal heat exchanger (INTREX), 7 – separator of solids, 8 – convective superheater and reheater, 9 – economizer, 10 – air preheater,11 – electrostatic precipitator (ESP), 12 – secondary fuel crusher

3.2. Chamber study

Smog chamber at UNC

The experiments with oil shale fly ash aerosol were performed in a dual outdoor Teflon film smog chamber (270 m^3) at University of North Carolina (UNC) Ambient Air Research Facility near Pittsboro (USA) (Fig. 2). The dual chamber

is Quonset hut in shape, with a width of 8.53 m, a length of 9.75 m and a height of 3.89 m [64, 65]. A suspended 5 mil (125 microns) DuPont™ Teflon® FEP film (type C) curtain (livingstone Plastics, Charlotte, NC) bisects the chamber to form two chamber halves. Sampling took place through manifolds that run directly to a laboratory beneath the chambers, and aerosol in the chamber moves ~1.5 m before reaching aerosol sizing instruments and filter samplers.

Figure 2. The dual outdoor Teflon Film smog chamber of UNC at Chapel Hill (NC, USA)

Chamber experiments with oil shale fly ash were conducted under normal meteorological conditions (temperature, humidity, sunlight), which were comparable to Estonian summer. The chamber leak rate, including sampling was between 1–5% per hour, as measured by a sulphur hexafluoride tracer. The chamber was purged with rural background air prior to experiment. The chamber was mixed for 2 min with the internal chamber fans after the fly ash particles was added and then the fans were shut off.

Particle size and number were monitored during the experiment with four different aerosol particle counters:

- TSI model 3071 connected with Ultrafine Condensation Particle Counter TSI model 3025A; (14 nm – 600 nm)

- TSI model 3080 Electrostatic Classifier connected with TSI model 3022A Condensation Particle Counter; (20 nm – 900 nm)
- TSI model 3321 Aerodynamic Particle Sizer® (APSTM) spectrometer (500 nm – 20 μm)
- Grimm aerosol spectrometer, Model 1.109; (250 nm – 32 μm)

The experiment started by injecting 1 g of PF and CFB oil shale fly ash into the two separate chambers. The particle mass and number concentration was monitored during the experiment for particles with size range from 14 nm to 32 μm using different analyzers and sampling systems.

Smog chamber at Tuulna

For this study and for a comparison of the results obtained from the smog chamber at UNC, an outdoor smog chamber (108 m^3) was built in Tuulna, Harju County, Estonia (Fig 3). The chamber is cube shape with a width of 6 m, a length of 6 m and a height of 3 m. The chamber walls and ceiling was covered with 2 mil (50 microns) DuPont™ Tedlar® PVF film from inside. Tedlar® 2 mil film was used because of its non-stick and chemically inert properties. From outside it was covered with 1mm thick PVC to avoid the breakup of Tedlar® film by the wind. As the sunlight does not have any effect to the particle size distribution the outside cover was negligible.

Figure 3. Outdoor smog chamber at Tuulna, Harju County, Estonia.

Sampling took place through manifolds that run directly to a laboratory beneath the chamber. The distance between air/fly ash suspension injection spot and aerosol sizing instruments was ca 1.0 m. The chamber was purged with filtered rural background air prior the experiment. The chamber was mixed for 2 min with the internal chamber fans after fly ash injected and then the fans were shut off.

Particle size and number distribution was measured with two different aerosol particle counters:

- Dekati Electrical Low Pressure Impactor (ELPI™) (0.030 – 10 μm) (Fig. 4) connected with vacuum pump Sogevac SV65B
- Grimm aerosol spectrometer, Model 1.109; (250 nm – 32 μm)

Figure 4. Dekati Electrical Low Pressure Impactor

3.3. Water extraction procedure

The selected leaching test, the European standard EN 12457 Part 2 (1999) [66], belongs to the so-called shake tests, which the maximum leachable amount is investigated at the material's own pH value. The test was applied as a sequential batch leaching of ash fractions with two extractions in deionized water, with

liquid/solid ratio of 10 l/kg for both extractions. The fly ash (60 g) was shaken in sealed glass bottles with 600 ml of water for 24 h. The liquid and the solid phase were separated by filtration through a 0.45 μm filter (HIMIFIL). The ash was quantitatively returned to the bottle, fresh deionized water was added, and the leaching/filtration procedure was repeated.

The parameters determined in leachates were pH, conductivity, and the concentration of total mineral and organic matter in the water phase. The pH and conductivity of the water extracts of the samples were measured immediately using a BENCH PC 510 pH/Conductivity Meter (Oakton Instruments, USA). The electrode was calibrated with pH buffer solutions before each determination. The concentration of mineral and organic matter was determined after evaporation of the extract in a water bath and drying in a vacuum drier (STP–200, Poland). The dry residue was found at 105 °C (2 h), the mineral and organic parts at 400 °C (4 h) until constant mass of residue was obtained. From the hazardous organic compounds, the set of US Environmental Protection Agency (EPA) priority PAH (Table 3) was determined by extraction of the water phase with 10 ml of n-hexane. The solvent was evaporated until the end volume under N_2, and 2 ml of acetonitrile was added and subjected to the high performance liquid chromatography (HPLC).

3.4. PAH chemical analysis

The ash samples were Soxhlet extracted for 20 hrs with acetone-hexane (50:50 by vol). The extracts (ca 150 ml) were evaporated to ca 1 ml in rotary evaporator at 53°C and 400-500 mbar. The PAH fraction was separated in a glass column (8 ml), filled with Silica gel 60 (0.040-0.063 mm, 230-400 mesh ASTM), equilibrated with n-hexane and fractionated by n-hexane/dichloromethane (1:1). The fraction containing PAH was reduced to 2 ml under N_2, transferred into an automatic sampler vial and subjected to the HPLC analysis.

The HPLC system HP 1100 consisted of a vacuum degasser, a gradient pump, an automatic sampler, a column thermostat, a diode array detector, a fluorescence detector, and a computer workstation (Agilent Technologies, Germany). The priority PAH was separated with an acetonitrile gradient at 308 K and 0.5 ml/min. The separation started with 58% acetonitrile, the content of organic solvent was increased to 100% in 35 min and finally held at 100% acetonitrile for the last 12 min. The analytical column parameters were MZ-PAH C-18.5 μm, 250 mm, 3 mm I.D (MZ Analysentechnik, Germany).

3.5. Trace metal analysis

Ash samples (0.27 g) were digested in concentrated ultra pure grade HNO_3. Digestion of the samples was performed in an Anton Paar microwave oven with a program running at 1000 W for 1 minute, followed by 350W for 10 minute.

Digested samples were diluted directly in the vessel to 76.8 ml volume with distilled water and then further diluted to 0.1M HNO_3. Final diluted water was decanted into Falcon type 14 ml polypropylene (pp) tubes for determination by an Inductive Coupled Plasma High Resolution Mass Spectrophotometer (ICP-HR-MS).

The HR-ICP-MS was selected for the trace metal analysis because of its capability to perform multielemental analysis with low detection limits. The analysis was performed in the Institute of chemistry at the Norwegian University of Science and Technology (NTNU), using Thermo Element 2 (ICP-HR-MS). An argon plasma burning at 6000 - 10 000K was maintained by introducing approx. 1200W power from an RF-generator. Elements analyzed included (Fe, K, Mg, Mn, Ca, Cd, Ce, Co, Ni, Cr, Cu, Ti, V, Pb, Th, U, Sm, Pr, Hg, Tl, Zn, Rb, Sr, Mo, Sn, Sb, Ba, La).

The absolute detection limits ranged from 5 pg for Cd to 15 ng for Ca.

4. RESULTS AND DISCUSSION

4.1. Atmospheric behavior and aging of fly ash

Deposition of fly ash particles, determined through the fractional size distribution, enables us to assess the behavior of the aerosol in the atmosphere. It allows calculation of the lifetime of different aerosol fractions in the atmosphere and an assessment of the possible impact to human health and ecosystems.

The particle count data obtained from the aerosol sizing instruments at the UNC chamber study showed that the total settling of fractions with diameter of particles less than 10 μm takes several hours (Fig. 5 and Fig. 6). The number concentration of the fine fractions (particle diameter less than 0.5 μm) was higher than bigger fractions (diameter of particles between 0.5 μm and 10 μm) (Fig. 6).

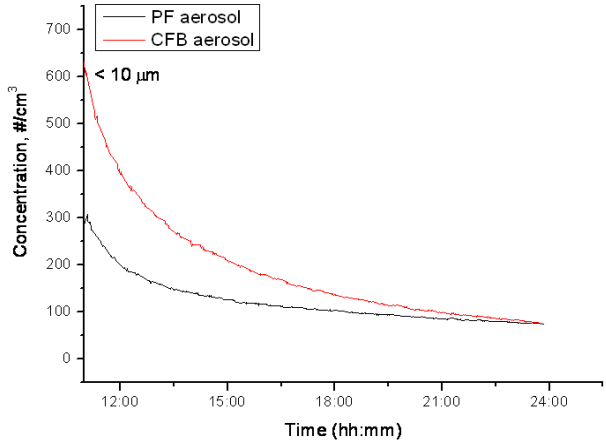


Figure 5. Number concentration of PF and CFB aerosol less than 10 μm.

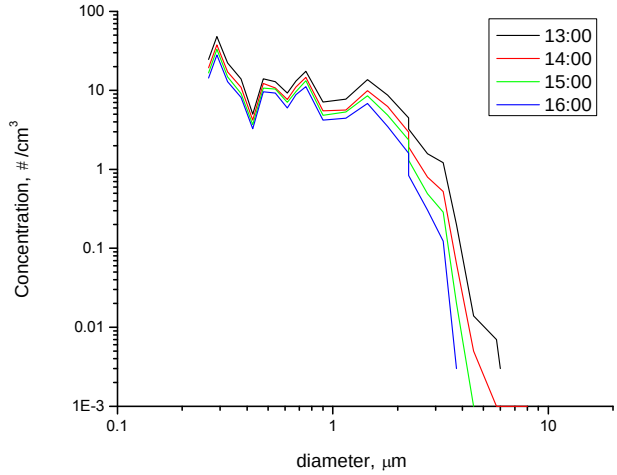


Figure 6. Number concentration of CFB fly ash.

For a better understanding the particle count data was calculated into mass. The initial aerosol mass concentration decreased quickly due to the deposition of larger particles (Fig. 7 and Fig. 8). From fractional distribution of CFB fly ash a trimodal PSD was observed (Fig. 7). The highest concentration was measured for the particles with diameter around 4 µm and the higher concentrations were determined for the particles with diameter around 2 µm and 3 µm. It can be also seen that particles larger than 4 µm in diameter are settled during about two hours, but particles with size about 2 µm are still hovering after 4 hours, although their concentration was decreased about 5 times from 250 µg/m^3 to 50 µg/m^3 (Fig. 7). For PF fly ash the fractional distribution (Fig. 8) was similar to the distribution of CFB fly ash.

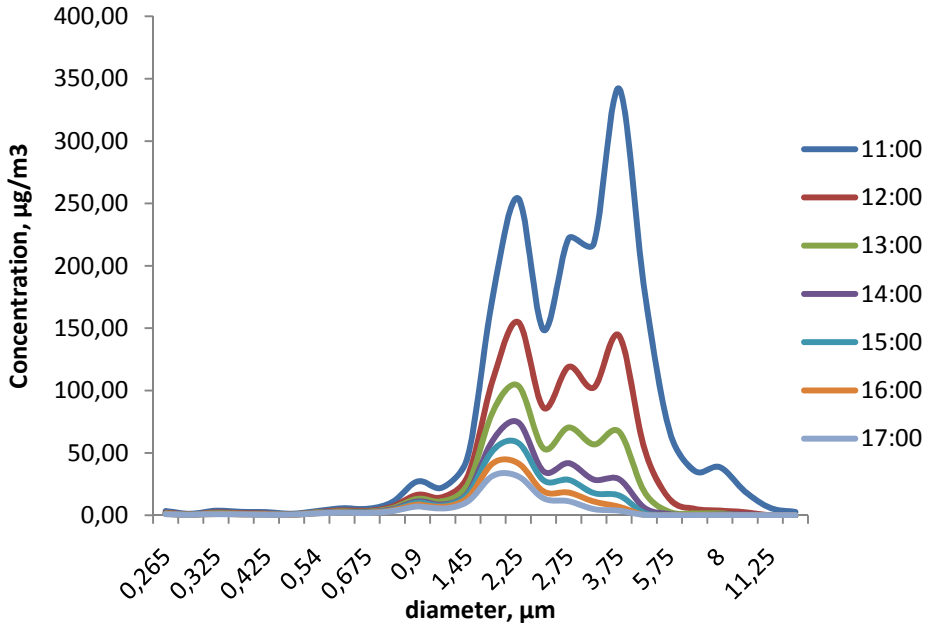


Figure 7. Fractional distribution of CFB fly ash in 2008.

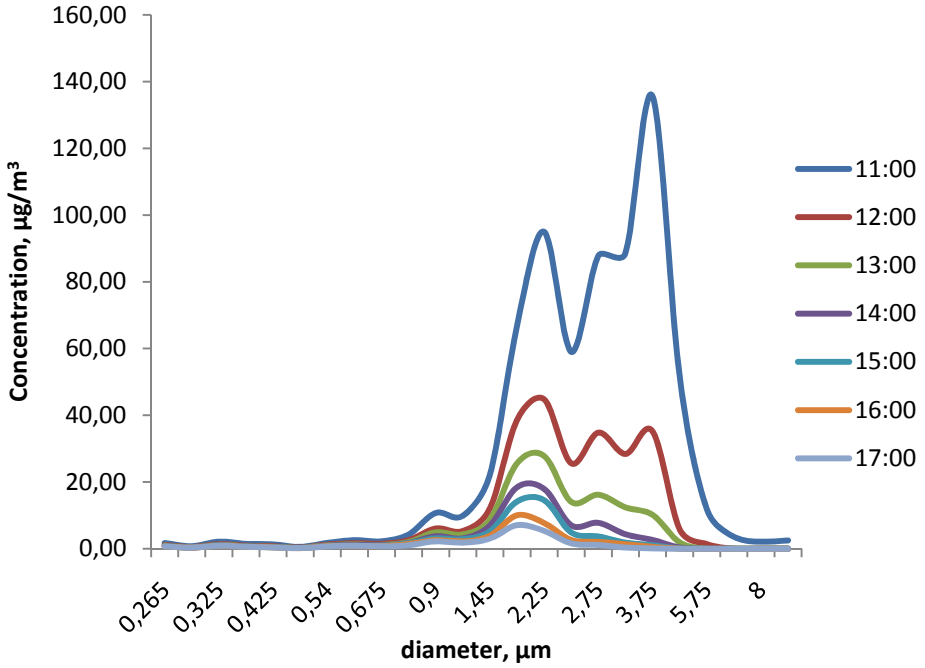


Figure 8. Fractional distribution of PF fly ash in 2008.

Fractional distribution obtained from the experiments in 2010 in the smog chamber at Tuulna deviate slightly from the 2008 experiments (Fig. 9). The highest concentration of particles was found with a diameter around 4 µm, but there were more particles with diameter around 0.5 µm than in results obtained in 2008. The reasons for this deviation of results could be that there has been some combustion technology adjustment during the two years period of time, and/or the oil shale combusted is originated from different mines. Similar fractional distributions were found for both CFB and PF fly ash aerosol emitted to chamber, although the CFB fly ash formed has different compositional and morphological properties compared with the PF ash [17,18].

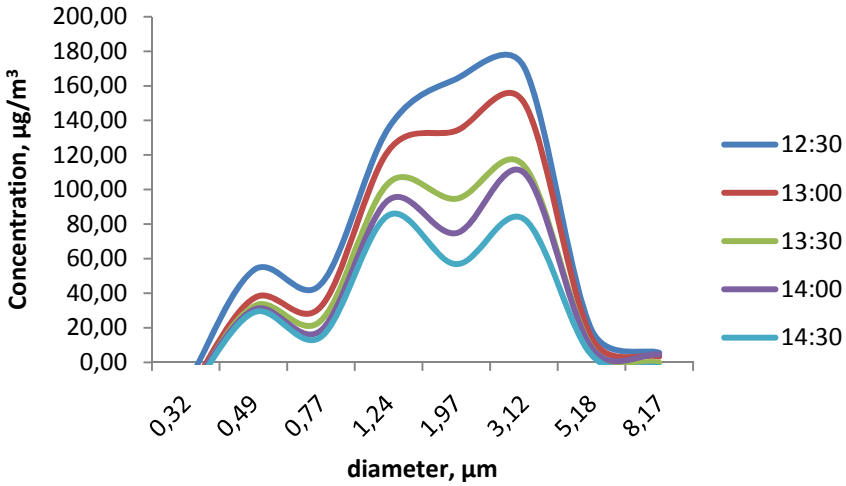


Figure 9. Fractional distribution of CFB fly ash in 2010.

One set of experiments was also made in high humidity conditions (over 95% humidity). The size distribution of the particles was about the same but the settling time of the aerosols were drastically faster than with previous experiments made in normal weather conditions. Most of the fly ash particles settled in less than 10 minutes (Fig. 10). This shows that weather conditions have a substantial impact in the deposition and transport of the fly ash aerosols formed.

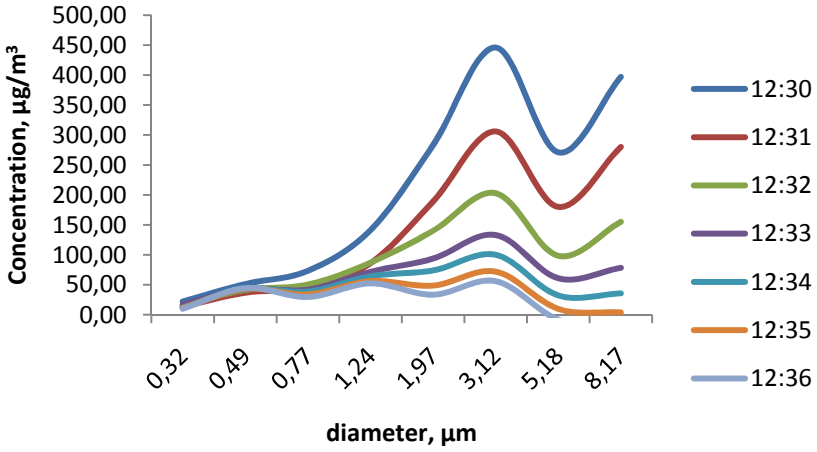


Figure 10. Fractional distribution of PF fly ash in 2010 in high humidity conditions.

From (Fig. 7 to Fig. 10) the results obtained it can be observed that a significant amount of coarse particles are settling close to the injection site. In real circumstances, the coarse fraction of fly ash emissions will be a local concern and will not have a significant regional impact.

The mass difference gap between analysis results from gravimetric analysis and automatic analyzers for PF fly ash is a result of the deposition of larger particles in the early stage of the experiment and was not determined by automatic analyzers. For both PF and CFB aerosols the total mass concentration was decreasing quickly due to deposition. The CFB aerosol had a relatively higher content of finer fractions than PF aerosol. The same result was also observed by Parve et al., where it was found that at in CFB combustion the share of the finest fraction PM 2.5 was higher than that at PF combustion [23].

The resulting stable aerosol with a mass median diameter around 2 μm was formed during over several hours. Therefore we can say that the fly ash from the PF and CFB combustion is forming stable aerosols, which are prone to long-range transport. Evidence of long-range transport of persistent pollutants, including PAHs, heavy metals, absorbed onto fine particles, has been investigated in many studies [25, 31].

Regarding the results obtained ultrafine particles with a diameter 0,5μm and less were also found in significant quantities. These particles could a greater hazard to human health, as they can reach terminal bronchi and alveoli of human lungs [67]. Studies that characterize the ultrafine particles illustrate that higher concentrations of hazardous and volatile elements occur in the ultrafine fractions than in either the coarse or fine fractions, with enrichments of up to 50 times observed for some elements [36].

Koukouzas et al. [56], and Jankowski et al. [58] have observed that coal fly ash shows bi-modal particle size distribution with the main peak at 4 μm and a secondary peak between 0.2 and 0.3 μm.

The particle size distribution is an important property of fly ash, with the smaller particles having greater surface areas. Size distribution is important during the interaction of the ash with different solutions, since it affects the mobilization of any trace elements on the surface of the particles. Chemical and physical properties vary greatly as a function of the particle size distribution of ashes.

Knowledge of the size distribution of fly ash particles is a useful tool for modeling the dry deposition.

4.2. PAHs

Results of chemical analysis of ash fractions are presented in Table 4 and 5. The different PAH compounds, included in the US EPA Priority List (Table 3), were identified in the extracts of the ash samples. Acenaphtylene, a relatively light representative of PAH from the Priority List was not found in the ash extracts. The total concentration of PAH in the ash fractions was found to be in the range of 82.2-152.1 μg/kg, including BaP, 7.9–15.1 μg/kg for the PF process whereas for the new CFB technology (Table 5), the total content of PAH was lower, 30.2-63.7 and 2.6-6.4 for BaP. The average mean content of PAH in all ash fractions studied was 107.8±29.6 μg/kg for PF and 47.0±11.0 μg/kg for the CFB system. These results are in agreement with the literature's data [47],

indicating that the particulate PAH emission for the CFB process tested appears to be lower than those typically reported for conventional coal combustion technology.

Table 4. Content (μg/kg) of individual PAH compounds in oil shale ash fractions Combustion by PF technology (boiler 5, Estonian PP).
Abbreviations, see Table 3

Abbreviation	Electrical precipitators		
	I unit	II unit	III unit
NA	10.11	12.99	7.11
AC	2.55	3.18	2.02
FL	2.71	4.12	2.10
PHE	4.26	7.39	3.95
AN	3.92	7.54	3.35
FA	5.30	9.29	5.50
PY	6.07	10.99	5.93
BaA	6.82	11.97	6.53
CHR	8.85	15.12	8.48
BbF	6.88	12.40	6.62
BkF	0.00	0.00	0.00
BaP	8.35	15.12	7.89
DBahA	7.50	13.53	7.33
BghiP	8.85	16.21	8.69
IP	6.84	12.24	6.77
Total PAH	89.00	152.11	82.24

Table 5. Content (μg/kg) of individual PAH in oil shale ash fractions Combustion of oil shale by CFB technology (boiler 8, Estonian PP)
Abbreviations, see Table 3

Abbreviation	Electrical precipitators			
	I unit	II unit	III unit	IV unit
NA	2.93	4.95	2.46	3.03
AC	1.57	1.57	1.31	2.07
FL	1.65	1.93	1.22	2.20
PHE	2.85	3.13	2.05	3.99
AN	2.12	3.14	1.24	2.94
FA	2.54	4.11	2.11	2.45
PY	2.87	4.47	2.02	3.54
BaA	3.20	5.03	2.29	4.11
CHR	3.93	6.76	2.74	4.56
BbF	3.26	5.13	2.34	4.39
BkF	0.00	0.00	0.00	0.00
BaP	3.95	6.41	2.75	5.25
DBahA	3.52	5.58	2.49	4.43
BghiP	4.07	6.48	2.90	5.17
IP	3.23	5.03	2.26	4.12
Total PAH	41.69	63.70	30.18	52.24

It is well known that individual PAH differ substantially in their physico-chemical properties. The vapor pressures of PAH range in five to twelve orders of magnitude (Table 3). The various conditions of PF and CFB should lead to different behavior of PAH compounds in the process of combustion. The most abundant individual compounds for both technologies applied were DBahA, BaP, and CHR, which all could be characterized as heavy PAH with low vapor pressure ($<10^{-7}$ Pa) and boiling points over 448°C (Table 3). The lower molecular mass compounds were present in much smaller quantities. The relative amount of heavy PAH was found to be more significant in the PF process compared to the CFB technology. The relationship between the degree of mutagenic activity and the presence of heavier PAH, i.e., masses 252 Dalton and over, was clearly illustrated by multiple authors [41]. On the other hand, the relatively higher amount of light PAH derivatives could indicate that, when applying to the CFB technology, the reactions of pyrolysis are more pronounced, whereas for the PF technology the pyrosynthesis is supposed to be the prevailing process in PAH formation. Figure 11 illustrates the comparison of individual PAH, from the last ESP of both combustion processes.

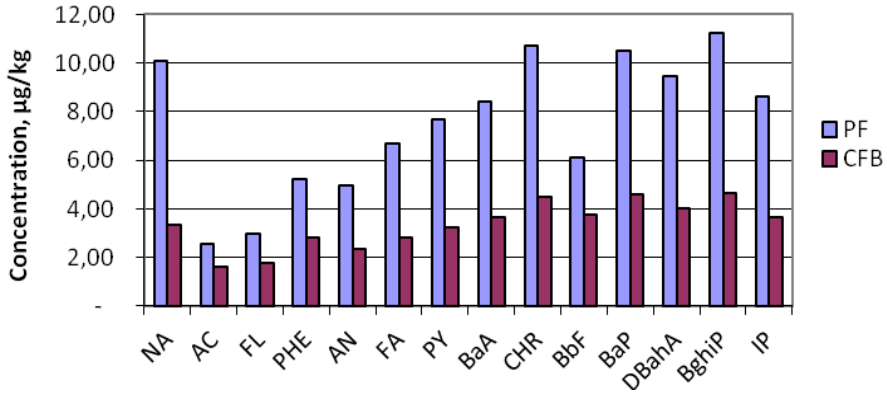


Figure 11. Comparison of individual PAHs, from the last ESP of PF and CFB combustion processes.

4.3. Leaching behavior of ash

The leachate water of all ash samples studied was very alkaline; pH values were in the close range (12.68–12.76). It is not surprising, because the content of Ca in any forms in oil shale and ash was found to be significant [68]. The dissolution of CaO and $Ca(OH)_2$ results to the high initial production of alkalinity. The relative potential of ash fractions to produce alkaline solutions depends primary on the CaO content, which is very high in oil shale itself [68]. Similar pH values, e.g., 12.0–12.3 for water extracts of ash samples are characteristic also for some coals (PF combustion) [52, 69].

At the same time, the conductivity (mS cm^{-1}) of water extracts of ash samples studied was in the range of 119–137 and 108-117, in the first and second stages of leaching tests, respectively. The conductivity of water phase in leaching of coal ashes has been found in the range of 167 to 505 mS cm^{-1} [52, 70].

The release of total mineral ingredients from ash samples is illustrated in Figure 12. It is clearly seen that the inorganic components were released from the CFB ash in both stages of extraction, whereas for the PF process this was, predominantly during the first stage of leaching. A good agreement between the conductivity values and contents of mineral matter in different leachates was observed, see above and Figure 12.

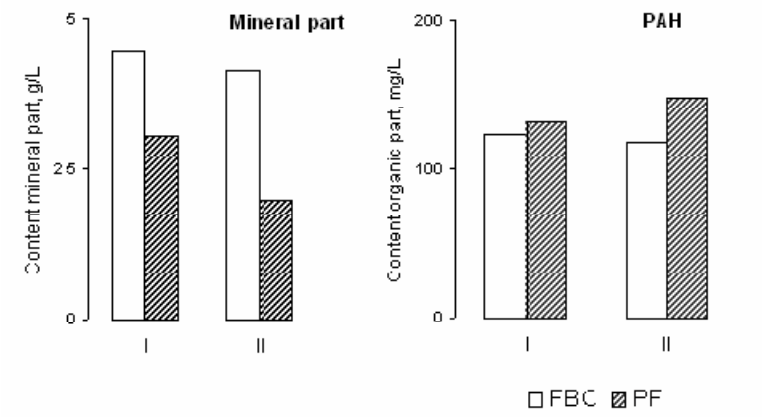


Figure 12. Total release of mineral components and PAH during two-step leaching (I and II stage) of ash samples of oil shale combustion by PF and CFB technologies.

The distribution of identified individual representatives of priority PAH in leachates of PF and CFB fly ash (Figures 13 and 14) demonstrates the different behaviors of these compounds in water extraction.

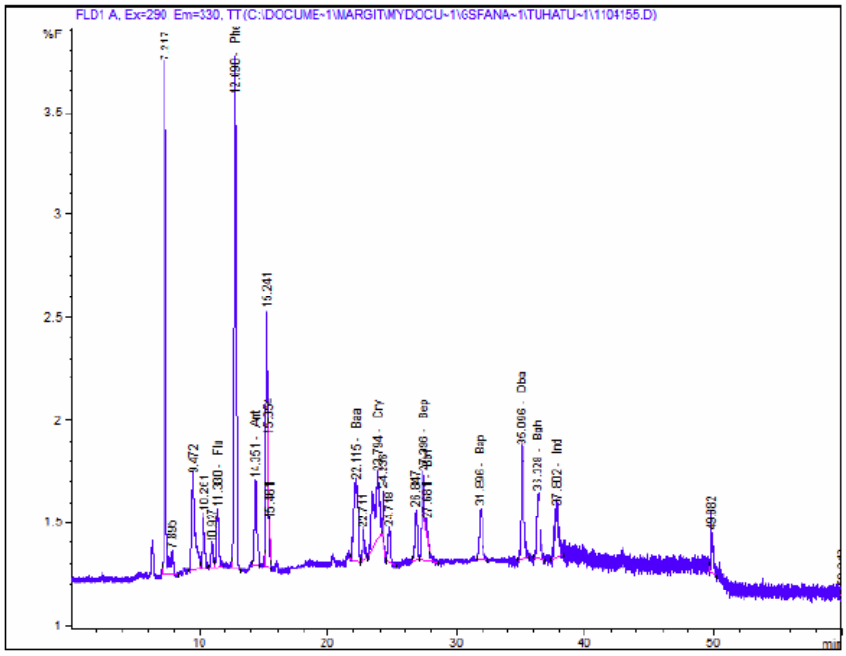


Figure 13. Distribution of PAH compounds in unit III of ESP ash of PF process in first water leachate.

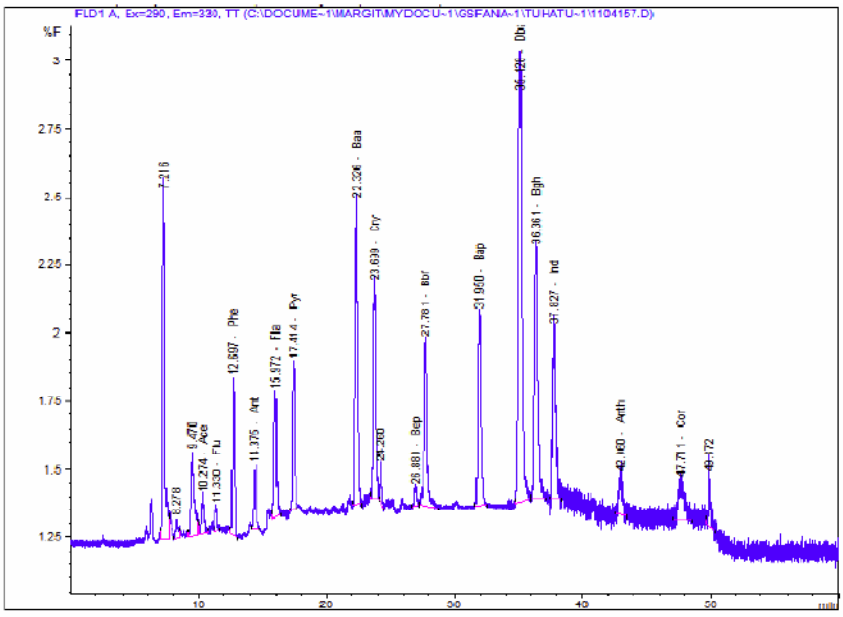


Figure 14. Distribution of PAH compounds in unit IV of ESP ash of the CFB process in the first water leachate.

The identification of a significant fraction of very hydrophobic PAH compounds in the water phase of ash samples was an important finding from the point of view of the environmental impact of deposited ash. However, the results for the ash samples generated in the CFB process were different (Figure 14). The high content of heavy PAH in water extract was somewhat worrying because these compounds were found to be more dangerous than the light ones [38].

The public health risks associated with oil shale wastes is connected mainly to their leachates. The behavior of PAHs in water extracts of fly ash samples of PF and CFB depends on the technological processes applied.

4.4. Heavy metals

Luan et al., has presented a Synthesis Toxicity Index (STI) model to perform the toxicity assessment of present and potential contamination caused by heavy metals with different fractions and quantities [28]. Previous studies show that the bio-available fraction of metals decreases with time and with an increase in pH, clay and organic matter contents [71, 72]. In the STI model, it is suggested that organic matter have a negligible impact on potential toxicity and that pH exerts a great influence on the valid toxicity of heavy metals. The toxicity coefficient T_r, used in STI model, reflects an ecosystem's sensitivity to the pollution caused by heavy metals [73]. The toxicity coefficient for heavy metals like Zn, Cu, Ni, Cr, Pb, Cd as well as melting and boiling temperatures are given in Table 6 [28].

Table 6. The STI toxicity coefficient of selected heavy metals and their melting and boiling points.

Heavy metal	Mp ^{o}C	Bp ^{o}C	T_r
Zn	420	907	1
Cu	1083	2567	5
Ni	1453	2732	5
Cr	1857	2672	3
Pb	327	1740	5
Cd	321	765	30

The concentrations of heavy metals in different fractions of oil shale fly ash were measured by Thermo Element 2 ICP-HR-MS. The results presented in Table 7 for PF combustion technology are coherent with previously published results of Aunela-Tapola et al. [61].

Table 7. Heavy metal concentrations (μg/g) and relative standard deviation (%) from PF combustion.

	Pb	Cd	Zn	Cu	Ni	Cr
Bottom ash	14.5	0.1	62.8	8.0	17.1	16.9
	1.9	*5.2*	*1.2*	*1.7*	*0.9*	*0.9*
Superheater	37.9	0.3	55.8	9.9	18.3	20.8
	1.4	*3.4*	*3.3*	*2.8*	*3.1*	*1.7*
Cyclone	29.4	0.1	45.6	35.0	19.1	18.7
	1.4	*4.0*	*2.3*	*1.5*	*1.8*	*1.4*
El. precip field I	73.2	0.3	81.5	8.0	21.9	37.1
	1.8	*1.9*	*1.0*	*0.9*	*2.5*	*0.5*
El. precip field II	136.3	0.6	142.1	14.6	32.8	59.0
	1.5	*1.7*	*0.6*	*0.9*	*3.7*	*0.5*
El. precip field III	141.6	0.9	143.2	12.2	28.4	50.6
	1.3	*1.4*	*1.3*	*1.5*	*0.7*	*0.4*

Table 8. Heavy metal concentrations (μg/g) and relative standard deviation (%) from CFB combustion.

	Pb	Cd	Zn	Cu	Ni	Cr
Bottom ash	24.2	0.1	41.4	8.3	21.4	19.7
	0.6	*6.1*	*2.0*	*1.5*	*0.4*	*1.2*
Intrex	29.2	0.1	50.7	7.4	25.4	29.3
	0.6	*3.2*	*2.8*	*2.8*	*2.6*	*2.2*
El. precip field I	78.3	0.1	56.0	12.4	39.6	53.9
	1.1	*2.6*	*4.2*	*1.3*	*3.8*	*2.4*
El. precip field II	21.6	0.1	38.4	7.7	19.7	19.6
	1.6	*5.3*	*2.2*	*2.0*	*1.2*	*2.0*
El. precip field III	85.0	0.2	55.4	14.2	44.2	59.9
	0.9	*2.0*	*3.3*	*1.0*	*0.6*	*2.6*
El. precip field IV	65.2	0.1	53.5	13.9	40.6	52.0
	1.1	*2.1*	*2.6*	*1.1*	*0.3*	*1.3*

As can be seen from Figure 15 and 16 the concentrations of Pb and Zn are higher in the ash from the last precipitator of the PF boiler compared to the CFB. This phenomenon can be explained by the fact that the firing temperature in the PF boiler is higher (1500 ^{o}C) compared to that of the CFB (800 ^{o}C) [4, 5]. Previous studies showed that the elemental contents of fly ash, which were close to the melting and boiling points of the elements (metals or compounds), increased (see Table 6). In general, the lower the melting and boiling points for either elements or compounds (oxides, sulfates and chlorides), the higher the contents of the corresponding elements in the fly ash [74].

As compared to CFB ash, the concentrations of selected toxic heavy metals in PF ash are higher (Table 8), except for Cd. The concentrations of Cd in ash samples from both boilers remain low compared to other heavy metals of interest.

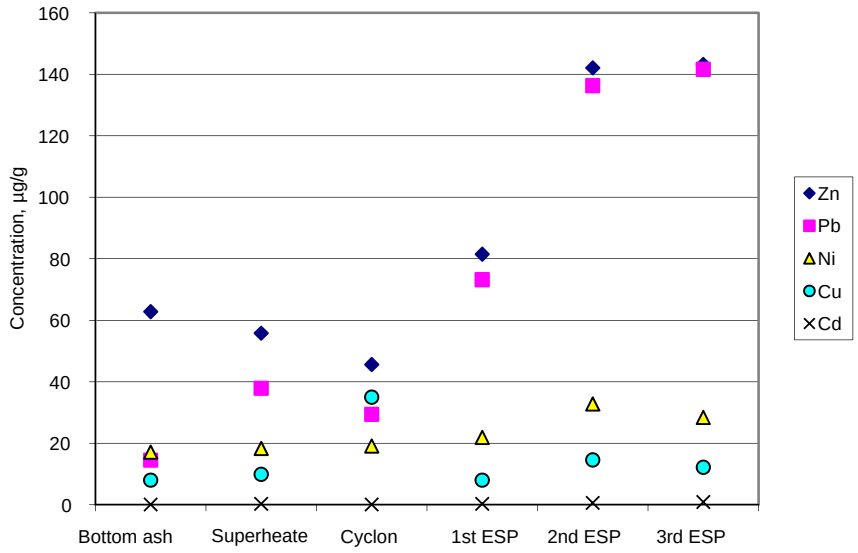


Figure 15. Concentrations of selected heavy metals in different PF ash fractions.

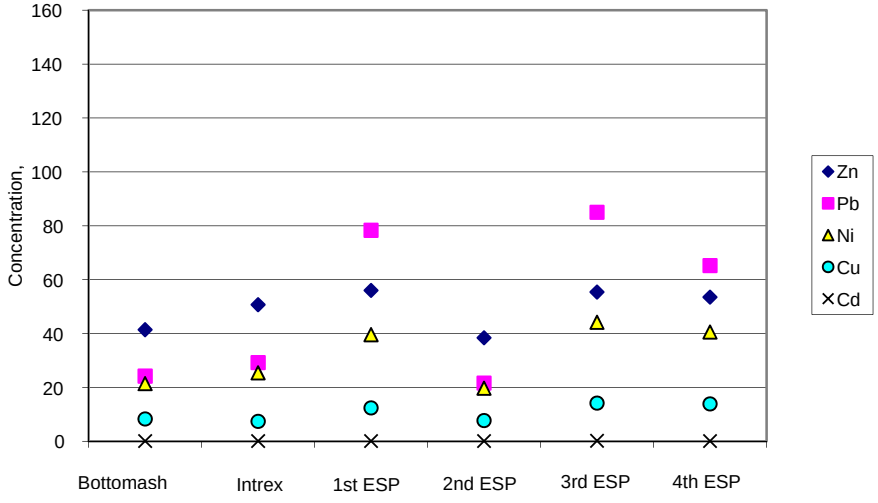


Figure 16. Concentrations of selected heavy metals in different CFB ash fractions.

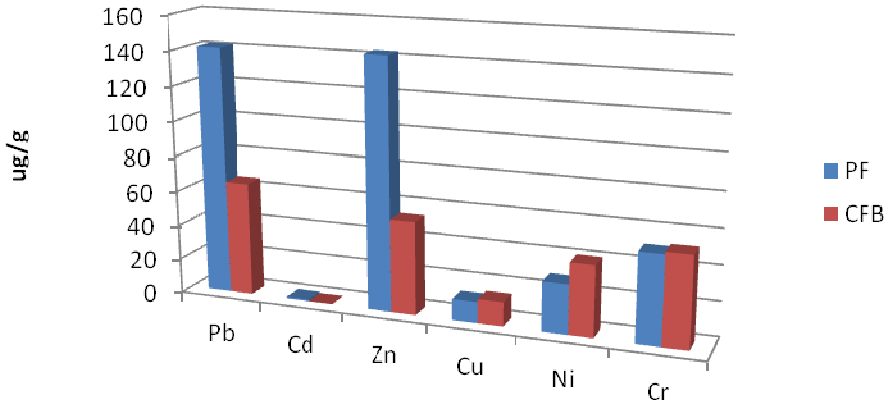


Figure 17. Comparison of selected heavy metals from PF and CFB combustion ash from the last unit of ESPs.

The results show a clear accumulation of Pb, Cd, Zn, Cu, Ni and Cr on fly ash along the gas duct. This observation was also found in the work of Aunela-Tapola et al. [61].

The difference between concentrations of elements might be that elements having lower boiling point (Pb, Zn), except for Cd, are more volatilized (Table 6). Concentration of heavy metals in fly ash is higher as compared to bottom ash, except for Zn and PF ash. The finding can be explained by the fact that the specific area of the ash particles increases along with the gas purification system. The traces of heavy metals are absorbed onto surface of ash particles. Koukouzas et al. [56] also found that the samples that have the highest trace element concentration were also those with the finest particles. No difference was found between the fly ash and bottom ash samples due to the difference in the mass of the elements like suggested by Sushil et al. [75].

CONCLUSIONS

Fly ash discharged by PF and CFB technology from Estonian PP was compared in this work. Special emphasis was addressed to polycyclic aromatic hydrocarbons (PAH) and toxic heavy metals. Investigation of difference in atmospheric behavior of the fine particles was made. Also leaching test according to European Standard EN 12457–2 was carried out.

The total concentration of PAH in the ash fractions was found to be in the range of 82.2-152.1 μg/kg, including BaP, 7.9-15.1 μg/kg for the PF process whereas for the new CFB technology, the total content of PAH was lower, 30.2-63.7 μg/kg and 2.6-6.4 μg/kg for BaP.

According to the leaching test the water extracts of different ash samples were very alkaline with similar pH values. The high conductivity values and high concentration of mineral components in the water indicates a significant water solubility of inorganic ingredients of oil shale ash. Organic components, including hazardous PAH, were also found in water extracts. A continuous release of mineral and organic compounds to the water phase was detected with two-phase leaching tests. The amount of soluble mineral matter in the first and the second water extracts was significantly higher in the CFB process, as compared to the PF technology.

The total concentration of hazardous organic pollutants, PAH in CFB ash is lower than in PF ash. However, from leaching tests of the ash, the cumulative release of PAH, was more significant in CFB process than in the PF process. Therefore the environmental hazard of deposition of solid wastes would be more pronounced in the CFB process than in the conventional PF technology.

The properties and aging behavior of the fly ash aerosols from PF and CFB process had similar properties and behavior in the simulated chamber study. Initial fly ash aerosol had multimodal fractional distribution with mass mean diameters around 2 μm and 5 μm. Both the PF and the CFB fly ash formed during the aging process stable aerosol with mass median diameter around 2μm which is prone to long-range transport. Based on the experimental results obtained in this study with oil shale fly ash aerosol, we can conclude that the new CFB technology does not provide better performance comparing to the PF technology, from an environmental point of view.

There was a notable accumulation of heavy metals such as Pb and Zn in the oil shale fly ash collected from the last electric precipitator of the boiler operating on the PF technology. The high concentration and toxicity of the heavy metals in the fly ash can cause environmental problems and is an obstacle to the direct application without any treatment.

As a result of the current study valuable knowledge of the impact of the solid waste from oil shale PPs on the environment was obtained.

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SUMMARY IN ESTONIAN

Elektri tootmisel tekkiva põlevkivituha keskkonnamõju – keevkiht- ja tolmpõletustehnoloogia

Igasugune kütuse põletamine on potentsiaalne saasteainete allikas. Põlevkivi põletamine tekitab suures mahus erinevaid jäätmeid, nii gaasilisi kui tahkeid. Samuti on teada, et tekkivad tahked jäätmed erinevad nii oma omadustelt ja koostiselt sõltuvalt põletatavast kütusest ja põletustehnoloogiast. Ühe tonni põlevkihi põletamise tagajärjel võib tekkida kuni pool tonni tahkeid jäätmeid, ehk tuhka.

Käesoleva doktoritöö eesmärgiks oli uurida põlevkivielektrijaamast pärinevate tahkete osakeste ehk tuha mõju keskkonnale võrreldes omavahel tolmpõletus- ja keevkihtpõletustehnoloogiat. Töö käigus teostati uuringud, mis kirjeldavad lendtuha aerosooli käitumist atmosfääris, tuhaosakeste settimiskiirust ning polüaromaatsete süsivesinike (PAH) ja raskmetallide sisaldust põlevkivielektrijaama lendtuhas, samuti põlevkivituha käitumist veega kokkupuutel. Tuhaproovid pärinesid AS Narva Elektrijaamad kahel erineval tehnoloogial põhineva põletamisprotsessi tuhakogumispunktidest.

Atmosfäärsete saasteainete uuringud viidi läbi suurtes atmosfääriosakeste uuringute kambrites nii USAs kui Eestis. Uuritud tuhkade fraktsioonilised jaotusomadused ja käitumine ajas oli suhteliselt sarnane. Mitmemodaalse jaotusega tuhaosakeste suurused olid peamiselt vahemikus 2–5 µm. Suuremad osakesed settisid väga kiiresti, enamasti paari tunniga. Väiksemad osakesed aga olid stabiilsemad. Võib eeldada, et väiksematel osakestel on potentsiaal lenduda tuulega kaugemale. Kamberuuringute tulemustele lähtudes võib väita, et osakeste lenduvuse ja jaotuse poolest, ei ole keevkihttehnoloogia keskkonnaseisukohalt parem kui tolmpõletustehnoloogia.

Kogu PAH sisaldus uuritud tuhafraktsioonides jäi tolmpõletusprotsessi puhul vahemikku 82,2–152,1 µg/kg, samas kui keevkihttehnoloogiast pärineva tuha PAH sisaldus oli madalam, jäädes vahemikku 30,2–63,7 µg/kg.

Teostatud leostuskatsetele vastavalt Euroopa standardile EN 12457–2, leiti et mõlema põletusprotsessi tuha vesiekstraktid olid väga leeliselised. Kõrged juhtivuse väärtused ja mineraalosa kontsentratsioon vesiekstraktis viitavad põlevkivituhas leiduvate anorgaaniliste ühendite suurele lahustuvusele. Märkimisväärsel hulgal leostus põlevkivituhast välja PAHe. Leostustesti kaheetapiline rakendamine tõestas, et põlevkivituhast erinevate saasteainete eraldumine vesifaasi on pidev protsess.

Raskmetallide uuringutest leiti, et peenematel tuhaosakestel, mis pärinesid tomplõletustehnoloogia viimastest elektrifiltritest on märkimisväärne kontsentratsioon Pb ja Zn puhul. Samas aga keevkihttehnoloogia puhul on Pb ja Zn kontsentratsioonid madalamad tänu madalamale põletamistemperatuurile.

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PUBLICATIONS

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