

LEACHING BEHAVIOR OF ASH FRACTIONS FROM OIL SHALE COMBUSTION BY FLUIDIZED BED AND PULVERIZED FIRING PROCESSES

M. LAJA, G. URB, N. IRHA, J. REINIK, U. KIRSO*

National Institute of Chemical Physics and Biophysics
23 Akadeemia Rd., Tallinn 12618, Estonia

Impact of solid wastes from an oil shale-fired power plant (near the town of Narva, Estonia) is characterized in terms of leaching behavior. A standard test for leaching granular waste materials and sludges was used for characterization of ash fractions. Ash samples were collected from two boilers: one applying pulverized firing (PF), and the other one, installed recently, applying fluidized bed combustion (FBC) technology. Similar behavior of ash from both systems was established, however, the amount of soluble mineral matter was found to be significantly higher in FBC process. Cumulative emissions of hazardous organic pollutants, e.g. polycyclic aromatic hydrocarbons (PAH), were approximately the same for both stages of leaching. Heavy PAH, including carcinogenic benzo[a]pyrene, were detected in ash leachates of the first as well as the second stage of both technologies. However, in PF process, 7.4% of the initial amount of PAH was leached from ash samples, whereas a significantly higher amount, 15.5% was leached in the case of FBC technology. Thus, environmental hazard in deposition of solid waste from FBC process would be more significant than that from the conventional (PF) technology.

Introduction

At present the AS Narva Elektriijaamad (Narva Power Plants Ltd.) is the biggest facility in the world generating the energy from oil shale combustion. By current technology the ash formed is transported to the 40–45 m-high ash fields using wet ash disposal system [1]. Today there are about 250 million tonnes of oil shale ash deposited onto ash fields and 15–20 million m³ of highly alkaline (pH over 12) water are in the settling ponds covering an area about 20 km² [2]. The main problem related to the disposed ash is the permanent intake of slurry water, which carries ash from the plant to the pond.

* Corresponding author: e-mail uuve@kbfi.ee

The mineral part of oil shale ash consists mainly of CaO (30–60%) and SiO₂ (20–50%), also Al₂O₃, Fe₂O₃, K₂O, and MgO are present [3]. Fly ash of oil shale combustion contains also, to some extent, ingredients such as toxic heavy metals and organic compounds [1, 2, 4]. A small (less than 2%) organic fraction of ash includes several polycyclic aromatic hydrocarbons, PAH [5], some of which are considered highly mutagenic and/or carcinogenic [5]. Potentially toxic elements leached from fly ash can contaminate soil, groundwater and surface water [6–8]. To predict the environmental impact of ash disposal systems of oil shale combustion in Narva PP, it is important to learn which compounds could be released to the environment and to understand the processes involved [1]. 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.

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. Using 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 [6, 9–12]. Environmental hazard could be identified basing on quantitative estimation of leaching of the contaminants from the solid phase into solution [13–17].

There are a number of parameters that influence leaching behavior of a solid material. Therefore the composition of extracts is highly dependent on test conditions. The effect of pH is dominating because it has the major influence on the majority of chemical species, especially carbonates [9, 10]. The cation-exchange capacity, and contents of iron/aluminum oxide are also the important factors, which determine the fate of pollutants in terrestrial environment or waste disposal [6, 10].

The main objective of the current work was to investigate the behavior of ash produced by oil shale combustion in water extraction processes with special emphasis on the process technology. Ash samples were collected from two different combustion processes; one representing pulverized fuel (PF) technology, and the other one fluidized bed combustion (FBC) installed recently, both at Eesti PP (one from two separate plants of Narva PP). The work was focused on hazardous organic compounds, individual metals, salts and specific ions were not tested.

Experimental

Ash samples were collected at boiler No. 5 (PF technology) and boiler No. 8 (FBC technology) from Eesti PP. Both combustors were operating in steady state regime during the sampling episodes. The sampling from the both boilers was performed approximately at the same time. The characteristics of

the raw material (oil shale) were established, and ash was sampled by the specialists of Narva PP. The process characteristics were checked and found to be representative ones. The samples were transported to the laboratory in the next day after sampling and stored at cold conditions (4 °C) before their leaching and chemical analysis.

The leaching procedure most commonly used in Europe has been the German one-stage leach test DIN 38414 S4. Currently a new compliance test for leaching granular waste materials and sludges *European standard prEN 12457 Part 1–4 (November 1999)* with several extraction stages is being developed for characterization of waste. The selected leaching test, European standard prEN 12457 – Part 2 (1999), is a so-called shake test, in which the maximum leachable amount is being investigated at the pH value of the material.

The following procedure was applied: each ash sample (60 g) was leached with deionized water (liquid/solid ratio of 10 L/kg) during 24 hrs. At the end of extraction, the suspension was separated through a 0.45 µm filter (HIMIFIL, Estonia). The leachate was bottled and refrigerated until the analysis. The leachant was quantitatively returned to the flask, fresh portion of deionized water was added, and the leach/filtration procedure was repeated.

Properties of the 16 US-EPA PAH [14]

PAH	Number of rings	Aqueous solubility, mg/L	Log K_{ow}
Naphthalene	2	31	3.37
Acenaphthylene	3	16	4.00
Acenaphthene	3	3.8	3.92
Fluorene	3	1.9	4.18
Phenanthrene	3	1.1	4.57
Anthracene	3	0.045	4.54
Pyrene	4	0.13	5.18
Fluoranthene	4	0.26	5.22
Benz[a]anthracene	4	0.011	5.91
Chrysene	4	0.006	5.91
Benzo[b]fluoranthene	5	0.0015	5.80
Benzo[k]fluoranthene	5	0.0008	6.00
Benzo[a]pyrene	5	0.0038	5.91
Dibenzo[a,h]anthracene	6	0.0006	6.75
Indeno[1,2,3-cd]-pyrene	6	0.00019	6.50
Benzo[ghi]perylene	6	0.00026	6.50

The parameters determined in both leachates were pH, conductivity, and the content of total mineral and organic matter. pH and conductivity were determined immediately using a BENCH PC 510 pH/Conductivity Meter (Eutech/Oakton Instruments, USA). The electrode was calibrated using pH buffer solutions before each determination.

The content of mineral and organic matter was determined by evaporating the extract. Dry residue was established at 105 °C for the

mineral part, and at 400 °C in the case of the organic part, until constant mass of the residue was obtained.

As for the hazardous organic compounds, the set of US Environmental Protection Agency (EPA) priority PAH (the Table) was determined by extraction of the water phase with 10 ml *n*-hexane. The solvent was evaporated till the end volume under N₂, and 2 ml of acetonitrile was added. The PAH analyses were performed by High-Performance Liquid Chromatography (HPLC) system HP 1100 (Hewlett-Packard, USA) with a fluorescence detector, 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).

Results and Discussion

The leachate water of all ash samples studied was very alkaline; pH values were in a close range (12.68–12.76). It is not surprising, because the content of any forms of Ca in oil shale and ash was found to be significant [12]. Dissolution of CaO and Ca(OH)₂ results in high alkalinity of leachate. The relative potential of ash fractions to produce alkaline solutions depends mainly on CaO content, which is very high in oil shale itself [12]. Similar pH values, e.g., 12.0–12.3 for water extracts of ash samples, are characteristic also of some coals (at PF combustion) [7, 8].

At the same time, conductivity of water extracts of ash samples studied was in the range of 119–137 and 108–117 mS cm⁻¹, in the first and second stage of leaching, respectively. Conductivity of the water phase at leaching coal ashes has been found to be in the range of 167 to 505 mS cm⁻¹ [7, 13].

The release of total mineral ingredients from ash samples is illustrated in Fig. 1.

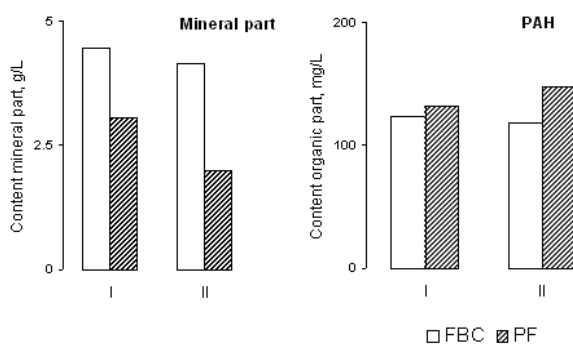


Fig. 1. Total release of mineral components and hazardous organic compounds (PAH) during two-step leaching (I and II stage) of bottom ash samples of oil shale combustion by PF and FBC technologies

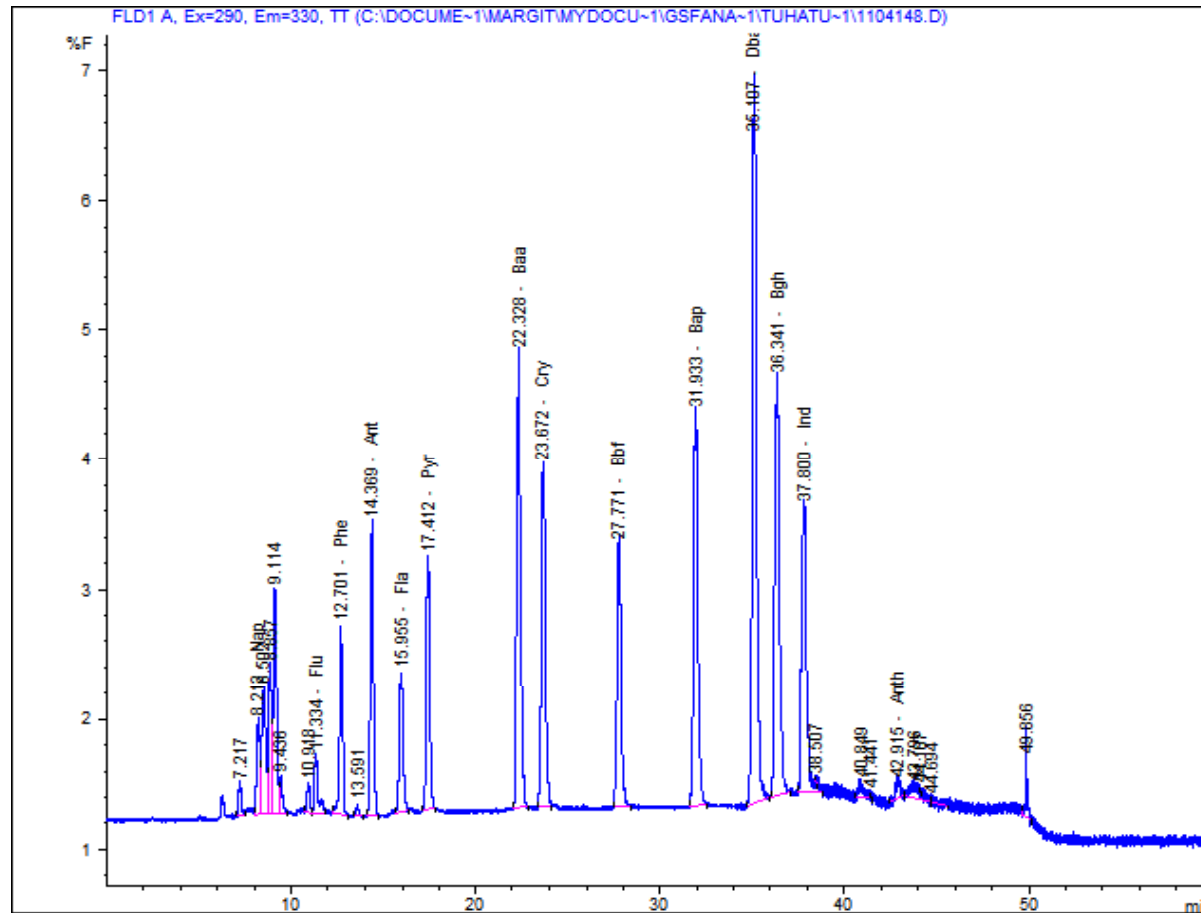


Figure 2-A.
Distribution of PAH
compounds in unit
III of electrostatic
precipitator's ash of
PF process

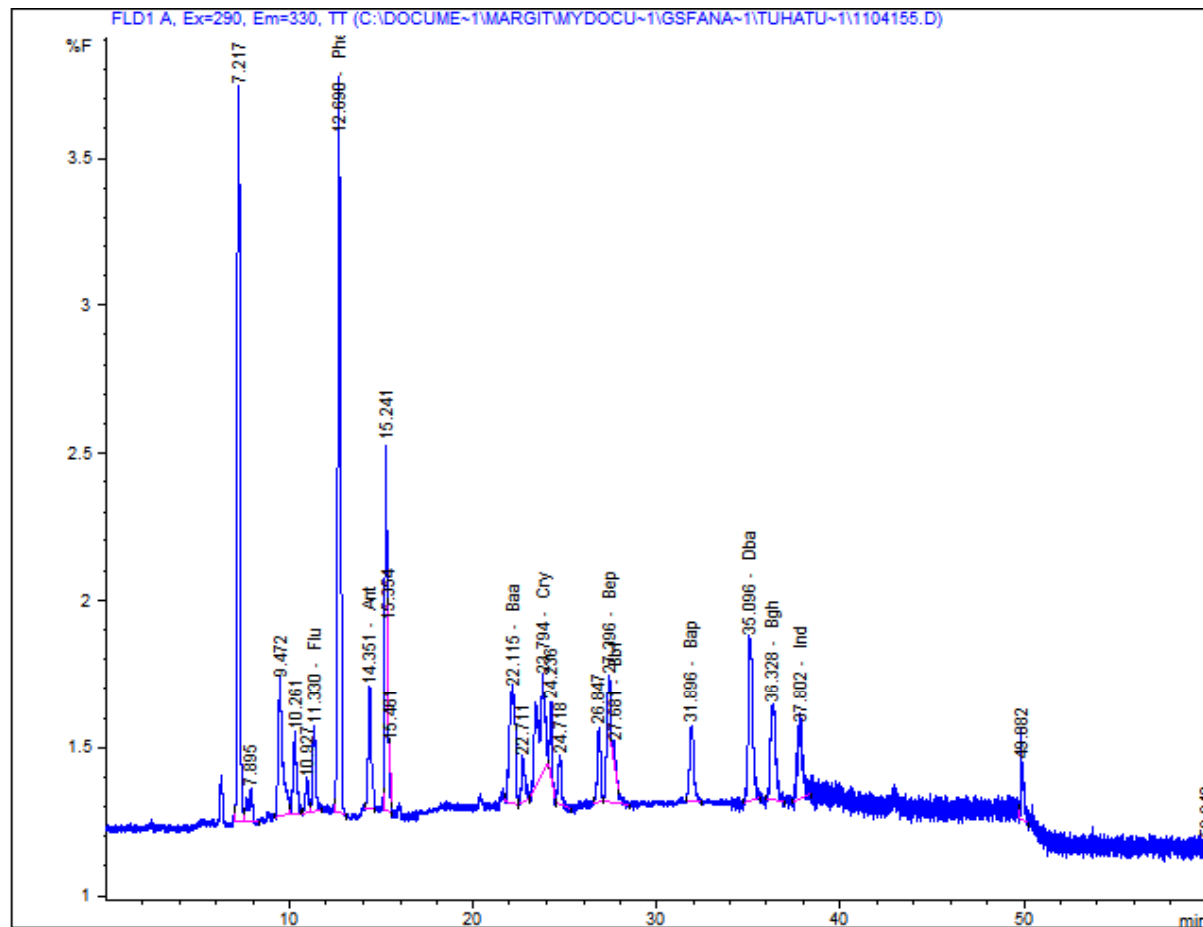


Figure 2-B. Distribution of PAH compounds in unit III of electrostatic precipitator's ash of PF process in first water extraction (leachate)

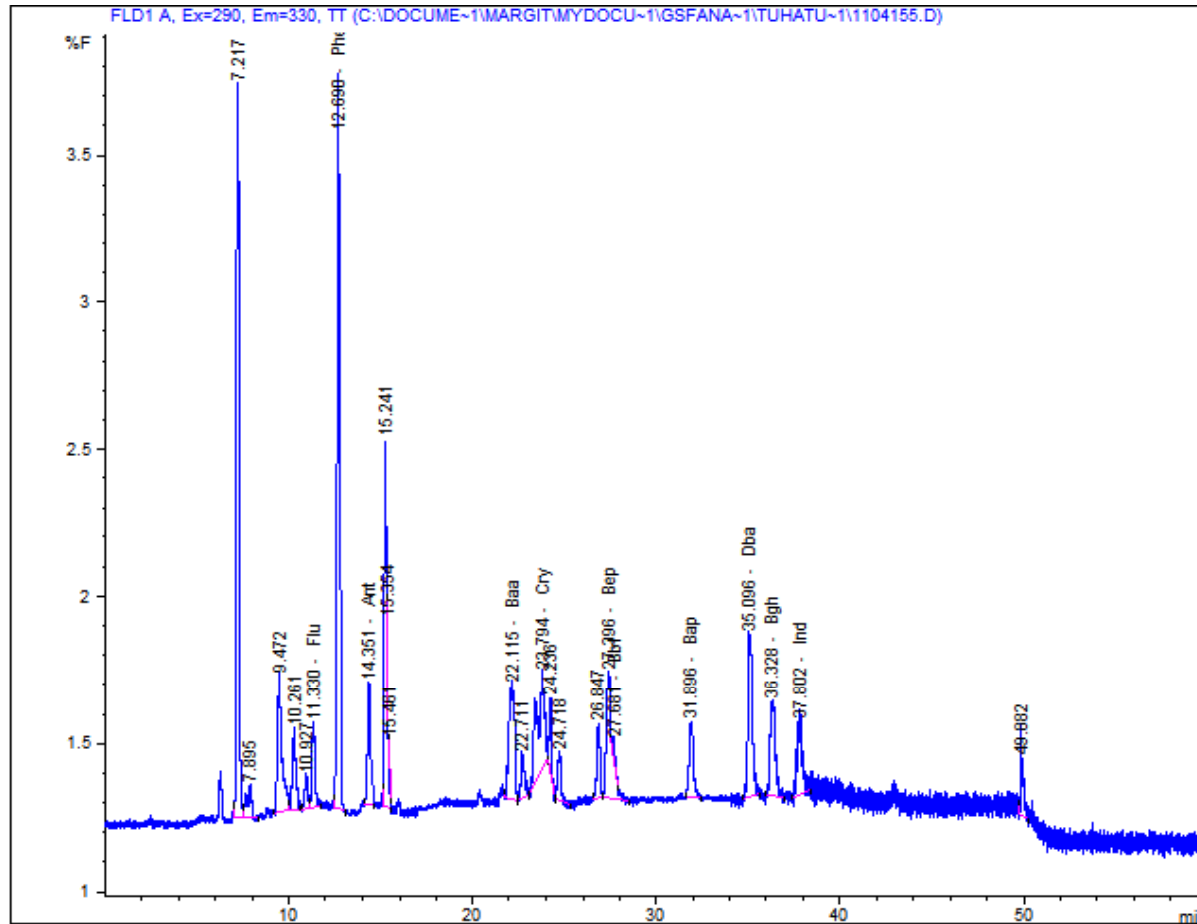


Figure 2-C.
Distribution of PAH
compounds in unit
III of electrostatic
precipitator's ash of
PF process in
second water
extraction (leachate)

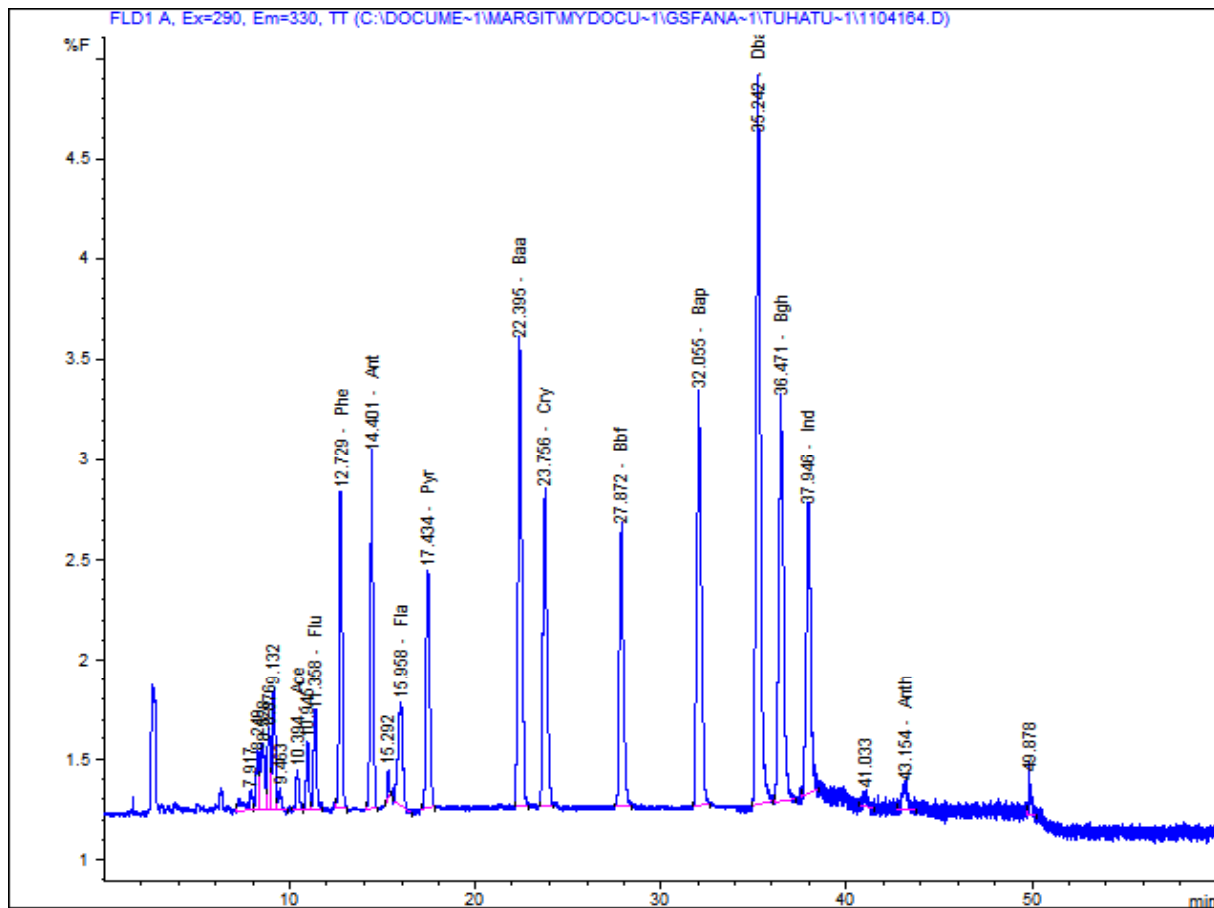


Figure 3-A. Distribution of PAH compounds in unit IV of electrostatic precipitator's ash of FBC process

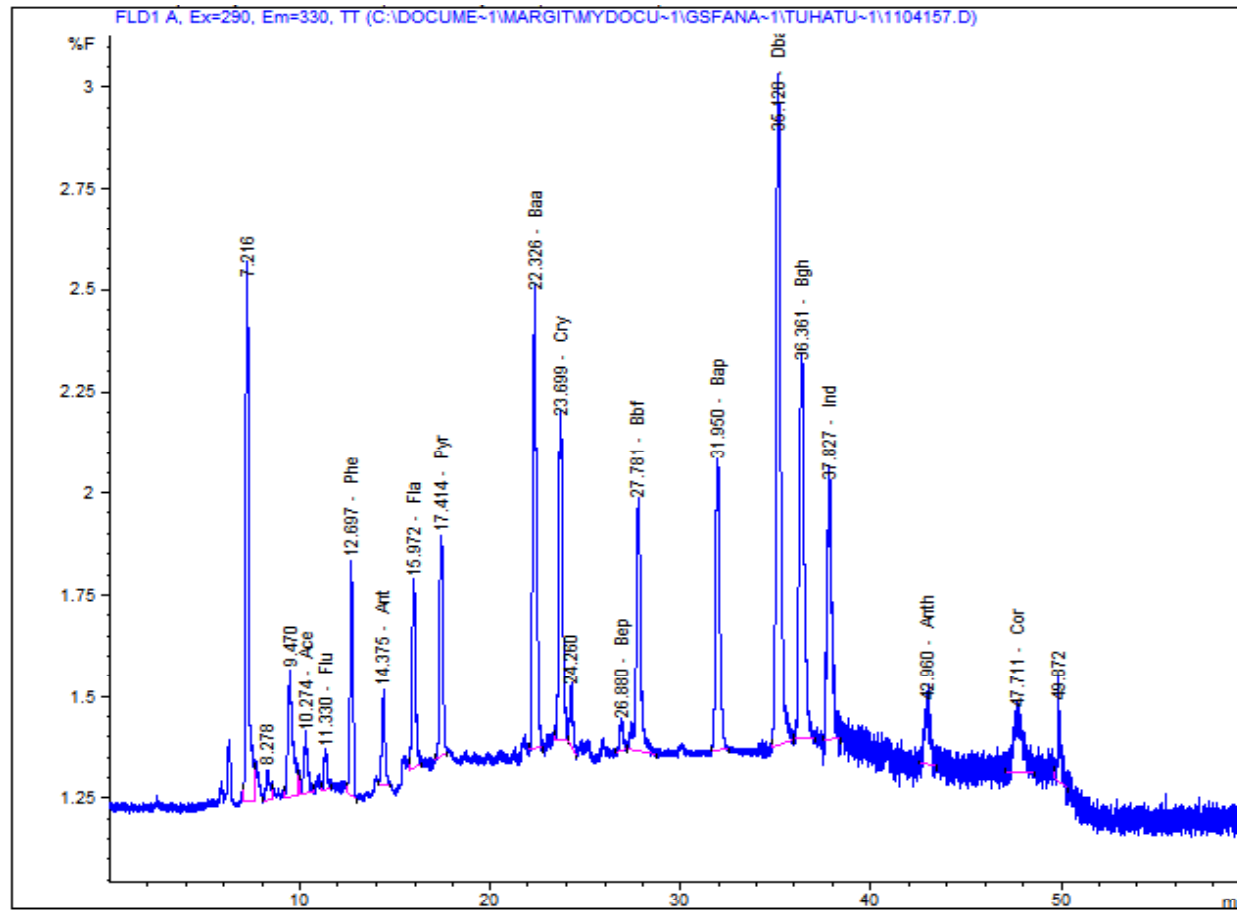


Figure 3-B. Distribution of PAH compounds in unit IV of electrostatic precipitator's ash of FBC process in first water extraction (leachate)

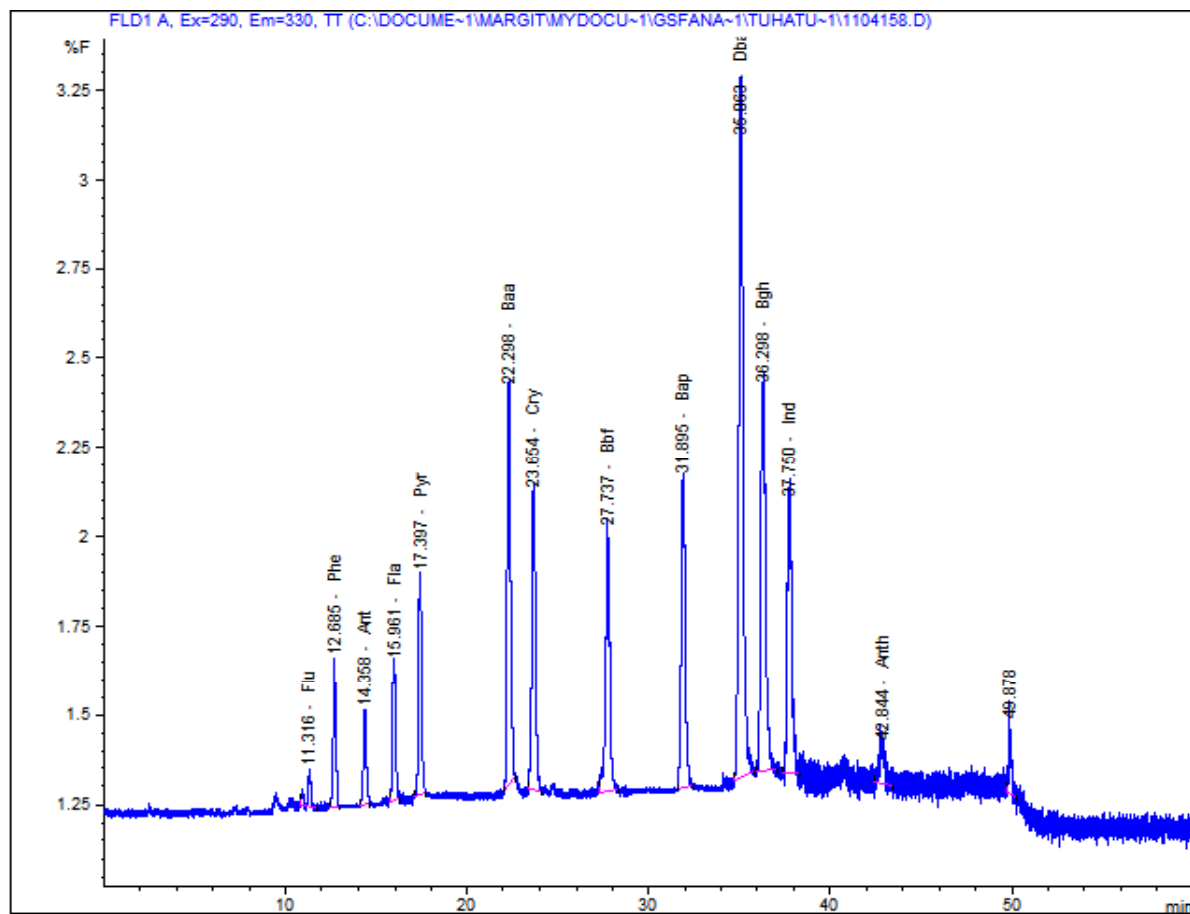


Figure 3. Distribution of PAH compounds in unit IV of electrostatic precipitator's ash of FBC process in second (C) water extraction (leachate)

It is clearly seen that inorganic components were released from FBC ash in both stages of extraction, whereas for PF process this happened predominantly during the first stage of leaching. A good agreement between the values of conductivity and content of mineral matter in different leachates was observed (see above and Fig. 1).

The identification of a significant fraction of very hydrophobic PAH compounds in the water phase of both extraction procedure of ash samples (Fig. 1) was an important finding from the point of view of environmental impact of deposited ash. The distribution of individual representatives of priority PAH in samples and corresponding leachates (Figs 2 and 3) demonstrates different behavior of these compounds during extraction with water.

The difference in hydrophobicity or solubility is also reflected by the octanol-water partition coefficient (K_{ow}) given in the table. As shown in this table, properties such as solubility in water and high affinity to organic matter (hydrophobic interaction) could largely determine the environmental behavior of PAH. It is clearly seen that the relative content of lower PAH was dominating in both leachates of ash samples from PF process (see chromatograms *B* and *C* in Fig. 2) compared to the initial distribution of individual compounds (see chromatogram *A* Fig. 2). However, the results for ash samples generated in FBC process were different (see Fig. 3). High content of heavy PAH in the first as well as in the second water extract (see chromatograms *B* and *C* Fig. 3) is somewhat worrying because these compounds were found to be more dangerous than the light ones [14, 17]. It is well known that public health risk associated with oil shale wastes is associated with their leachates [17].

Hence, the behavior of ash samples during leaching tests varied depending on the technological processes applied.

Conclusions

1. The amount of soluble mineral matter in the first and the second water extracts was significantly higher in FBC process, as compared to PF technology.
2. Cumulative release of hazardous organic pollutants, e.g. polycyclic aromatic hydrocarbons, was more significant in FBC process than in the traditional PF technology.
3. Environmental hazard of deposition of solid wastes would be more pronounced in FBC process than in the conventional PF technology.

Acknowledgements

Financial support from the project EST-02/003 according to bilateral cooperation in science and technology (WTZ) between Federal Ministry of Education and Research, Germany and Ministry of Education and Research, Estonia and Estonian Science Foundation (grant No. 5130) is gratefully acknowledged.

The authors would like to thank Narva PP, especially Mr. M. Uus and Mr. O. Parts, for providing representative ash samples and fruitful discussions, Dr. J. Lintelmann and MSc D. Antkowiak for the advice and support, Mrs. P. Laas for technical assistance.

REFERENCES

1. *Ots, A.* Technology of Oil Shale Combustion. – Tallinn, 2004 [in Estonian].
2. *Saether, O. M., Sørli, J. E., Kirso, U., Bitykova, L., Banks, D.* The chemistry and mineralogy of waste from retorting and combustion of oil shale // *Energy, Waste, and the Environment* / R. Gieré and P. Stille (eds.). A Geochemical Perspective, Geological Society. London, Special Publications. 2004. Vol. 236. P. 263–284.
3. *Raukas, A., Teedumäe, A.* Geology and Mineral Resources of Estonia. – Estonian Academy Publishers, Tallinn, 1997. P. 436.
4. *Õpik, I. P.* Ash utilization after combustion and thermal processing of Estonian (kukersite) oil shale // *Oil Shale*. 1989. Vol. 6, No. 3. P. 270–275.
5. *Kirso, U., Laja, M., Urb, G.* Polycyclic aromatic hydrocarbons (PAH) in ash fractions of oil shale combustion: fluidized bed *vers* pulverized firing process // *Oil Shale*. 2005. Vol. 22, No. 4S. P. 537–545.
6. *Teixeira, E. C., Binotto, R. B., Sanchez, J. D., Migliavacca, D., Fachel, J. M. G.* Environmental assessment and characterization of residues from coal processing and steel industry activities // *Fuel*. 1999. Vol. 78. P. 1161–1169.
7. *Choi, S.-K., Lee, S., Song, Y.-K., Moon, H.-S.* Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound // *Fuel*. 2002. Vol. 81. P. 1083–1090.
8. *Hansen, Y., Notten, P. J., Perie, J. G.* The environmental impact of ash management in coal based power generation // *Appl. Geochem.* 2002. Vol. 17. P. 1131–1141.
9. *Van der Sloot, H. A.* Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and field verification // *Waste Manag.* 1996. Vol. 16. P. 65–81.
10. *Sauve, S., Hendershot, W., Allen, H., E.* Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter // *Environ. Sci. Technol.* 2000. Vol. 34. P. 1125–1131.

11. *Querol, X., Umaña, J. C., Alastuey, A., Bertrana, C., Lopez-Soler, A., Plana, F.* Extraction of water-soluble impurities from fly ash // *Energy Sources*. 2000. Vol. 22. P. 733–750.
12. *Renton, J. J., Brown III, H. E.* An evaluation of fluidized bed combustor ash as a source of alkalinity to treat toxic rock materials // *Eng. Geol.* 1995. Vol. 40. P. 157–167.
13. *Moreno, N., Querol, X., Andrés, J. M., Stanton, K., Towler, M., Nugteren, H., Janssen-Jurkovicová, M., Jones, R.* Physico-chemical characteristics of European pulverized coal combustion fly ashes // *Fuel*. 2005. Vol. 84, No. 11. P. 1351–1363.
14. *Mackay, D., Shiu W.Y., Ma, K. C.* Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Vol. 2. Polycyclic Aromatic Hydrocarbons. – Chelsea: Lewis Publishers, 1992. P. 597.
15. *Baba, A.* Leaching characteristics of wastes from Kemerköy (Mugla-Turkey) power plant // *Global Nest: The Int. J.* 2000. Vol. 2, No. 1. P. 51–57.
16. *Lopes, H., Trindade, T., Gulyurtlu, I., Cabrita, I.* Characterization of FBC ashes from co-combustion of coal with oily residues // *Fuel*. 2001. Vol. 80. P. 785–793.
17. *Gratt, L. B.* Risk analysis of hazardous materials in oil shale // *J. Hazard. Mater.* 1985. Vol. 10. P. 317–350.

Received May 17, 2005