

## Characterization of water extracts of solid waste generated by oil shale combustion

*Dedicated to the 65th birthday of Professor Toomas Tenno, Chair of Colloid and Environmental Chemistry, University of Tartu*

Margit Laja<sup>a,b\*</sup>, Natalja Irha<sup>a</sup>, Gary Urb<sup>a,b</sup>, Janek Reinik<sup>a</sup>, and Uuve Kirso<sup>a</sup>

<sup>a</sup> National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia; natalja@kbfi.ee, urb@kbfi.ee, jreinik@kbfi.ee, uuve@kbfi.ee

<sup>b</sup> Institute of Physical Chemistry, University of Tartu, Jakobi 2, 51014 Tartu, Estonia

Received 4 April 2005, in revised form 4 May 2005

**Abstract.** This study focuses on the behaviour of oil shale combustion ash during water extraction processes. The oil shale ash samples were collected from two different combustion processes in Narva PP. The leaching tests of the ash samples were carried out in compliance with a European standard prEN 12457-2 (1999). The results show that both first and second water extracts are characterized by high alkalinity and conductivity and they contain polycyclic aromatic hydrocarbons.

**Key words:** oil shale fly ash, bottom ash, leaching.

### INTRODUCTION

Over 85% of the energy demand in the world is met by the combustion of fossil fuels such as coal, oil, and oil shale. However, use of the fossil fuels leaves its environmental footprint. The key environmental challenges due to the usage of fossil fuels are related to mining – principally the disturbance of landscape and the local human environment, as well as processing – greenhouse gases, acid rain, ground level ozone, and waste disposal issues. These impacts could be both of local or global scale.

The solid wastes that are generated by the combustion of solid fuels have widely varying composition depending on the fuel and combustion technology used [1–3]. The combustion of oil shale is accompanied by large quantities of solid residues. The environmental impact of solid waste, including ash and its utilization products, could be essential due to the mobility of hazardous substances.

---

\* Corresponding author, margit@kbfi.ee

In Estonia, two large thermal power plants (PP) with total electricity output of 3000 MW use oil shale [2, 4]. These PP in Narva contribute 60% of stationary energy in the country [5]. The current technology of processing oil shale is the combustion of pulverized fuel (PF). Recently a new, fluidized bed combustion (FBC) technology was introduced. Because of the high mineral content (60–95%) of the raw material [6], a large amount of ash (ca 45% of burned fuel) is generated. The mineral content of other fossil fuels, for instance brown coal, is considerably lower, i.e., 29%. The mineral part of the oil shale ash consists mainly of CaO (30–60%) and SiO<sub>2</sub> (20–50%), also Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, SO<sub>3</sub>, and MgO are represented [7]. The fly ash of oil shale combustion contains also to some extent ingredients such as toxic heavy metals and organic compounds [4, 8]. The small (less than 1.5%) organic fraction of ash includes several polycyclic aromatic hydrocarbons (PAHs), e.g., phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]- and benzo[*k*]fluoranthenes, benzo[*a*]pyrene, etc., some of which are considered highly mutagenic and/or carcinogenic [5, 8].

Most of the ash formed in Narva PP is transported to the 40–45 m high ash fields with a wet ash disposal system. About 250 million tonnes of oil shale ash has been deposited onto ash fields pro tempore and the settling ponds covering an area of about 20 km<sup>2</sup> have received 15–20 million m<sup>3</sup> of highly alkaline (pH 12–13) water [6]. The main problem of the disposed ash is the slurry water, which carries ash from the plant to the pond. Potentially toxic elements leached from fly ash can contaminate soil, groundwater, and surface water [9].

In general, the environmental impact of pollutants is related to their availability for transport and bio-uptake, rather than their total concentrations in the soil or waste material. Environmental hazard identification should therefore be made based on the quantitative estimation of the leaching of the contaminants from the solid phase into solution.

On the other hand, the mass transport of a chemical substance through soil and water is strongly affected by equilibrium between solid and aqueous phases. Evaluation of potential risks and toxicity of waste in a terrestrial ecosystem requires the assessment of the proportion of the total compound that is in a mobile and possibly bioavailable form. Use of a relatively simple extraction procedure, separation of phases, and chemical analysis of the water extract gives a solution to the problem. The term *leaching* is commonly used for the water extraction procedure in the environmental issues. The most popular water extraction procedure in Europe has been the German one stage leach test DIN 38414 S4. Currently a new procedure, a compliance test for the leaching of granular waste materials and sludges *European standard prEN 12457 Part 1–4 (November 1999)* with several extraction stages, is being developed for the characterization of waste. There are a number of parameters that influence the leaching behaviour. Therefore the composition of extracts is highly dependent on test conditions. The most important parameter is the value of pH, which depends mostly on the matrix composition. It is well known that liquid to solid ratio (L/S) also plays an important role in the extraction process [3, 10].

The main properties of coal combustion ashes and leaching characteristics are well studied [3, 11–14]. However, the authors failed to find any data in the literature about the systematic studies of leaching and solubility tests of oil shale wastes, including ashes. At the same time it is known that the coal combustion wastes have a high content of toxic trace metals [3, 11–13].

To predict the environmental impact of ash disposal systems of oil shale combustion facilities in Narva PP, it is important to know which compounds could be released to the environment in order to understand the processes involved [15]. Based on the information received in this work it is possible to characterize the hazard of wastes in site-specific conditions and transport and long-term changes in the utilization/disposal conditions.

This study focuses on the behaviour of ash produced by oil shale combustion in water extraction processes. The ash samples were collected from Narva PP.

## **EXPERIMENTAL**

### **Sample collection**

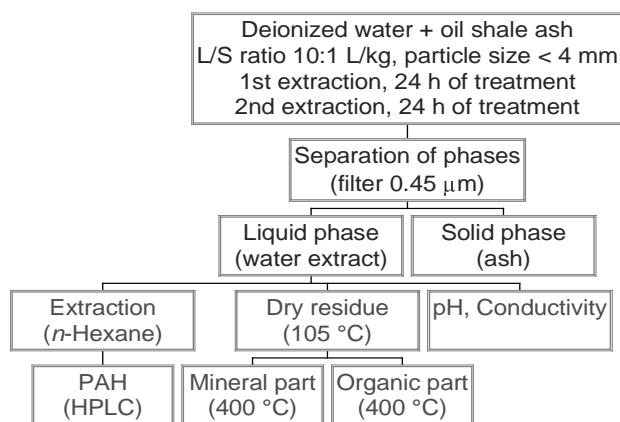
Ash samples were provided by Narva PP, which include Baltic PP and Estonian PP. The samples were collected at several locations of the gas flow duct of two different processes of oil shale combustion, i.e. PF technology and the recently installed FBC in Estonian PP (Table 1).

### **Water extraction procedure**

The selected leaching test, the European standard prEN 12457 Part 2 (1999), belongs to the so-called shake tests, in 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 each extract 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 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.

The overall scheme of the experimental part is illustrated in Fig. 1.



**Fig. 1.** Scheme of the water extraction procedure.

### Chemical analysis

From the hazardous organic compounds, the set of US Environmental Protection Agency (EPA) priority PAHs were determined by extraction of the water phase with 10 mL of *n*-hexane. The hexane in the samples was evaporated until the end volume under N<sub>2</sub>, and 2 mL of acetonitrile was added. The PAH analysis was performed by a high performance liquid chromatography (HPLC) system HP 1100 (Hewlett-Packard, USA) with a fluorescence detector. The PAHs were separated inside a column MZ-PAH C-18.5 μm, 250 mm, 3 mm I.D. (MZ Analy-sentechnik, Germany) at a column temperature of 308 K. Acetonitrile and water were used as the mobile phase with the flow rate of 0.5 mL/min. The gradient composition of the mobile phase started with 58% acetonitrile and was increased up to 100% in 35 min. This percentage was kept constant for 12 min until the end of the analysis.

All solvents used, acetone and dichloromethane (Merck, Germany), hexane and acetonitrile (Fluka, Germany), were HPLC or analytical grade.

## RESULTS AND DISCUSSION

It is well known that the pH, cation-exchange capacity, and iron and aluminum oxide contents are the most important factors that determine the fate of pollutants in terrestrial environment [12, 16]. The effect of pH is dominating because it has major influence on most chemical species, especially carbonate. The data presented in Table 1 show that the pH values of the first water extracts of the oil shale ash studied are similar and very high, whereas the conductivity values of the studied ashes changed on a large scale. For example, the conductivity of the electrostatic precipitator's (ESP) ash extract is 1.8 times higher than that of bottom ash extract. A difference is observed also in the conductivity values of both FBC and PF bottom ash extracts (Table 1).

**Table 1.** General characteristics of water extracts of different oil shale combustion ashes

Ash sample	First extraction		Second extraction	
	pH	Conductivity, $\mu\text{S cm}^{-1}$	pH	Conductivity, $\mu\text{S cm}^{-1}$
FBC bottom ash	12.74	12 290	12.69	11 540
PF bottom ash	12.68	7 770	12.73	10 850
PF cyclone ash	12.72	11 890	12.76	10 870
PF ESP, 1st unit	12.77	13 730	12.70	11 730

ESP – electrostatic precipitator.

**Table 2.** Characteristics of water extracts of some coal combustion ashes, data from [11, 17]

Object	Location	Combustion technology	pH	Conductivity, $\mu\text{S cm}^{-1}$
Lignite fly ash (ESP) [11]	Greece	PF	12.3	5050
Alkaline fly ash (ESP) [11]	The Netherlands	PF	12.2	4900
Sub-bituminous fly ash (ESP) [17]	South Korea	Nd	12.0	1668

ESP – electrostatic precipitator.

Nd – no data.

Table 2 compares the data of this study to the published characteristics of water extracts of selected coal combustion ashes obtained under the same conditions and L/S ratio [11, 17]. It is clear that the oil shale ash water extracts are characterized by higher alkaline pH and conductivity values (Table 1) than alkaline coal fly ash extracts (Table 2).

The pH values of the water extract of alkaline coal ash observed by Lopes and coworkers [14] are lower than the pH values obtained for oil shale bottom ash in this study. The data from [18] show that the FBC ash has a potential to produce solutions of high alkalinity due to the content of CaO and CaCO<sub>3</sub>. Querol et al. [19] demonstrated that the major phase inducing high alkalinity in the extraction experiment is free lime. Also a correlation between higher Al and Si concentration in the water extract and the higher alkalinity is evident. However, a large number of elements, such as the majority of heavy metals, have a very low mobility under alkaline conditions. As the pH of oil shale ash water extracts is very alkaline, one could predict that heavy metals in oil shale ash have low mobility [19].

It is interesting to point out that the content of lignite ESP fly ash is similar to the main composition of oil shale ash, including 28.5% SiO<sub>2</sub>, 17.9% Al<sub>2</sub>O<sub>3</sub>, and 27.3% CaO [11]. At the same time the conductivity of the water extract of lignite's ESP fly ash is 2.3 times lower than the conductivity of the oil shale ESP ash extract.

**Table 3.** Concentration of mineral and organic compounds (g/L) and PAHs ( $\mu\text{g/L}$ ) in water extract samples of bottom ash

Ash sample	Mineral part	Organic part	Total PAH
First extraction			
FBC	4.45	0.202	124.1
PF	3.08	0.043	132.2
Second extraction			
FBC	4.15	0.165	118.4
PF	1.97	Nd	148.2

Nd – no data.

The pH of the second water extracts of oil shale ash is characterized by very alkaline values that are close to the pH of the first extracts (Table 1). The conductivity values of the second extracts of all ash samples studied are similar. At the same time the conductivity of the water extracts of three ash samples have slightly decreased compared to the first extract, except the PF bottom ash. Hence, the behaviour of ash samples is different depending on the technological processes applied.

Comparison of the data of the sequential water extraction of oil shale ash obtained in this study to coal ash samples demonstrates that the leaching behaviour is different. According to the data in [17] the pH and conductivity of every next extract of coal ash are lower than in the previous extract. However, water extracts of oil shale ash are characterized by high values of pH and conductivity for both first and second extracts (Table 1).

In addition to the physico-chemical characteristics, the content of total mineral and organic ingredients in the water phase was determined (Table 3). A difference of more than an order of magnitude in the quantities of the organic compounds released was found between the two bottom ash samples.

The identification of a significant fraction of very hydrophobic PAH compounds in the water phase of both extraction procedures of bottom ash samples (Table 3) was the most important finding of the study from the aspect of the environmental impact of deposited ash.

## CONCLUSIONS

According to the results of this study, the following conclusions can be made:

1. The water extracts of different ash samples were very alkaline with close pH values.
2. The high conductivity values and high concentration of mineral components in the water phase indicate a significant water solubility of inorganic ingredients of oil shale ash.

3. Organic components, including hazardous polycyclic aromatic hydrocarbons, were also found in water extracts.
4. A continuous release of mineral and organic compounds to the water phase was detected.

### ACKNOWLEDGEMENTS

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

The authors would like to thank Narva PP for kind help and for providing the representative ash samples, Dr Jutta Lintelmann and MSc Dariusz Antkowiak for the advice and support, and Mrs Pilvi Laas for technical assistance.

### REFERENCES

1. Öpik, I. P. Ash utilization after combustion and thermal processing of Estonian (kukersite) oil shale. *Oil Shale*, 1989, **6**, 270–275.
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. In *Energy, Waste, and the Environment – A Geochemical Perspective* (Gieré, R. & Stille, P., eds.). *Geological Society, London, Special Publications*, 2004, **236**, 263–284.
3. Swaine, D. J. Composition and utilization of fly ash. In *Environmental Aspects of Trace Elements in Coal* (Swaine, D. J. & Goodarzi, F., eds.). Kluwer Academic Publishers, Dordrecht, 1995, 204–220.
4. Häsänen, E., Aunela-Tapola, L., Kinnunen, V., Larjava, K., Mehtonen, A., Salmikangas, T., Leskelä, J. & Loosaar, J. Emission factors and annual emissions of bulk and trace elements from oil shale fueled power plants. *Sci. Total Environ.*, 1997, **198**, 1–12.
5. Teinemaa, E. The environmental fate of the particulate matter and organic pollutants from an oil shale power plant. Doctoral Dissertation, University of Tartu, 2003.
6. Prikk, A. *Oil Shale Ash – Formation, Environmental Problems and Utilization, Research Report*. Tallinn University of Technology, Tallinn, 2004.
7. Raukas, A. & Teedumäe, A. *Geology and Mineral Resources of Estonia*. Estonian Academy Publishers, Tallinn, 1997.
8. Teinemaa, E., Kirso, U., Strommen, M. R. & Kamens, M. R. Deposition flux and atmospheric behavior of oil shale combustion aerosols. *Oil Shale*, 2003, **20**, 3S, 429–440.
9. Praharaj, T., Powell, M. A., Hart, B. R. & Tripathy, S. Leachability of elements from sub bituminous coal fly ash from India. *Environ. Int.*, 2002, **27**, 609–615.
10. Van der Sloot, H. A. Developments in evaluating environmental impact from utilization of bulk inert wastes using laboratory leaching tests and field verification. *Waste Manage.*, 1996, **16**, 65–81.
11. 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, **84**(11), 1351–1363.

12. 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, **78**, 1161–1169.
13. Baba, A. Leaching characteristics of wastes from Kemerköy (Mugla-Turkey) power plant. *Global Nest: Int. J.*, 2000, **2**(1), 51–57.
14. Lopes, H., Trindade, T., Gulyurtlu, I. & Cabrita, I. Characterization of FBC ashes from co-combustion of coal with oily residues. *Fuel*, 2001, **80**, 785–793.
15. Hansen, Y., Notten, P. J. & Perie, J. G. The environmental impact of ash management in coal based power generation. *Appl. Geochem.*, 2002, **17**, 1131–1141.
16. Sauvé, 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, **34**, 1125–1131.
17. 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, **81**, 1083–1090.
18. Renton, J. J. & Brown, H. E., III. An evaluation of fluidized bed combustor ash as a source of alkalinity to treat toxic rock materials. *Eng. Geol.*, 1995, **40**, 157–167.
19. 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, **22**, 733–750.

## **Põlevkivi põletamisel tekkivate tahkete jäätmete vesiekstrakti omadused**

Margit Laja, Natalja Irha, Gary Urb, Janek Reinik ja Uuve Kirso

On uuritud elektritootmisel tekkiva põlevkivituha käitumist veega kokkupuutel. Selleks teostati leostuskatsed vastavalt Euroopa standardile prEN 12457-2 (1999). Tuhaproovid pärinesid AS Narva Elektriijaamad kahel erineval tehnoloogial põhineva põletamisprotsessi katla- ja tuhaärastussüsteemist. Mõlema põletusprotsessi tuha vesiekstraktid olid väga leeliselised. Kõrged juhtivuse väärtused ja mineraalosa kontsentratsioon vesiekstraktis viitavad põlevkivituhas leiduvate anorgaaniliste ühendite suurele lahustuvusele. Märkimisväärset hulgal leostus põlevkivituhasst välja ka orgaanilisi ühendeid, sealhulgas ohtlikke polütsükklilisi aroomaatseid süsivesinikke. Leostustesti kaheetapiline rakendamine tõestas, et põlevkivituhasst erinevate saasteainete eraldumine vesifaasi on pidev protsess.