Realia et Realia naturalia

JEKATERINA JEFIMOVA

Leaching of polycyclic aromatic hydrocarbons (PAHs) and heavy metals from the oil shale processing wastes and from waste-based products

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22

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LIST OF ORIGINAL PUBLICATIONS

The thesis is based on original articles in peer-reviewed international research journals (hereafter referred to as Paper I – Paper VIII)

I   Joa, K., **Panova, E.,** Irha, N., Teinemaa, E., Lintelmann, J., Kirso, U. 2009. Determination of polycyclic aromatic hydrocarbons (PAHs) in oil shale processing wastes: current practice and new trends. Oil Shale, 26(1), 59–72.

II   **Jefimova, J.**, Irha, N., Mägi, R., Kirso, U. 2012. Application of Solid-Phase Microextraction Method to Determine Bioavailable Fraction of PAH in Hazardous Waste. Bulletin of Environmental Contamination and Toxicology, 89(4), 888–892.

III   Irha, N., Reinik, J., Steinnes, E., Urb, G., Kirso, U., **Jefimova, J.** 2013. Leachability of trace elements from aged and fresh spent shale deposit – a field study. Oil Shale, 30(3), 456–467.

IV   Reinik, J., Irha, N., Steinnes, E., Urb, G., **Jefimova, J.,** Piirisalu, E., Loosaar, J. 2013. Changes in trace element contents in ashes of oil shale fueled PF and CFB boilers during operation. Fuel Processing Technology, 115, 174–181.

V   **Jefimova, J.,** Irha, N., Reinik, J., Kirso, U., Steinnes, E. 2014. Leaching of polycyclic aromatic hydrocarbons from oil shale processing waste deposit: a long-term field study. Science of the Total Environment, 605–614.

VI   Reinik, J., Irha, N., Steinnes, E., Urb, G., **Jefimova, J.,** Piirisalu, E. 2014. Release of 22 elements from bottom and fly ash samples of oil shale fueled PF and CFB boilers by a two-cycle standard leaching test. Fuel Processing Technology, 124, 147–154.

VII   Irha, N., Uibu, M., **Jefimova, J.,** Raado, L.-M., Hain, T., Kuusik, R. 2014. Leaching behaviour of Estonian oil shale ash-based construction mortars. Oil Shale, 31(4), 394–411.

VIII Irha, N., Reinik, J., **Jefimova, J.,** Koroljova, A., Raado, L.-M., Hain, T., Uibu, M., Kuusik, R. 2015. PAHs in leachates from thermal power plant wastes and ash-based construction materials Environmental Science and Pollution Research, DOI 10.1007/s11356-015-4459-x.

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Author's contribution to the publications

Paper I: The author's contribution involved conducting the experiment with fluorinated PAHs, conducting GC-MS analysis, the interpretation of the results, the writing the paper (approximately 40%).

Paper II: The author's contribution involved SPME method development, conducting SPME-GC-MS analysis, the interpretation of the results, the calculation work and writing the paper.

Paper III: The author analyzed the results, performed the calculation work and wrote the paper (approximately 20%).

Paper IV: The author was responsible for the interpretation of the results and the calculation work.

Paper V: The author was responsible for GC-MS analysis of PAHs, the interpretation of the results, the calculation work and writing of the paper.

Paper VI: The author was responsible for the interpretation of the results and the calculation work.

Paper VII: The author was responsible for the interpretation of the results and the calculation work.

Paper VIII: The author was responsible for GC-MS analysis of PAHs, the interpretation of the results and writing of the paper (approximately 20%).

I. INTRODUCTION

Due to the increasing demand for energy, fossil fuels will continue to be the dominant source of primary energy production globally in the coming decades. Environmentally safe disposal and/or reuse of solid wastes are currently the key challenges related to the extensive use of fossil fuels (especially low-grade solid fuels). The largest industrially used oil shale basin in the world is based in Estonia. The two primary utilization pathways for oil shale are oil production by retorting and electricity generation by combustion. At present, two different oil shale retorting technologies are employed: the Kiviter type internal combustion vertical retort and the Galoter type or solid heat carrier unit (Veiderma, 2003). The Kiviter thermal processing of oil shale in Estonia started in 1924, whereas the Galoter retorting process has been employed since 1980 (Veiderma, 2003). Oil shale combustion at two of the world's largest oil shale-fired Thermal Power Plants (Eesti and Balti) started in 1959 and 1969, respectively. Until 2005, only pulverized-fired (PF) combustion technology was used. To improve the operational efficiency and to decrease the hazardous emissions, a new circulating fluidized bed combustion (CFB) technology was introduced in 2005. Currently, 20 PF boilers and 4 CFB boilers operate at the Thermal Power Plants (Bityukova et al., 2010). Due to the high content of mineral matter in oil shale a significant amount of oil shale processing waste is formed. 100 million tons of spent shale (also called semicoke) has been stored in piles and approximately 300 million tons of oil shale ash is deposited in gigantic ash fields in Ida-Viru. Only minor amount of oil shale processing wastes are reused: oil shale ash can be used in construction materials, agriculture and road building (Kuusik et al., 2005; Pihu et al., 2012).

The deposit and/or byproduct conversion of oil shale processing wastes may be detrimental for both the environment and human health because of entrained organic (polycyclic aromatic hydrocarbons – PAHs) and inorganic (heavy metals) pollutants. As oil shale processing wastes contain pollutants it is essential to assess which compounds and amounts could be released to the surrounding environment. Determination of mobile PAHs in the oil shale processing wastes is viable because many of them show carcinogenic and/or mutagenic properties. That is why the concentration of PAHs is regulated in most countries in the world. PAHs have a high affinity for organic matter and, when present in waste, soil or sediments, tend to remain bound to solid particles. PAHs can persist, transport and accumulate in the environment to the extent that the potential for adverse environmental effects is considerable (Alexander, 1995; Enell et al., 2004). Heavy metals deserve special attention because they have adverse effects on human health. Some of them are carcinogenic, mutagenic, teratogenic and endocrine disruptors, while others cause neurological and behavioural changes, especially in children. Heavy metals are nonbiodegradable and therefore accumulate in the environment. Many heavy metals can cause undesirable effects and severe problems even at very low concentrations (Arora et al., 2008; Memon and Schröder, 2009).

The quality of PAHs data generated with respect to accuracy and precision is critical for successful determination of criteria concentrations regulated by law. A particularly complicated task is the quantification of PAHs, because the first step of the PAHs' determination includes separation of the PAHs fraction from environmental matrices having very different physical-chemical composition and characteristics. It is stated that the main source of low quality of analytical data is often due to the sampling, pretreatment, and separation of analytes and not the final step, i.e. quantification of PAHs. Most methodologies for determination of PAHs in complex solid matrices such as soil, sediments or wastes are difficult to perform. It means that the traditional methods of sample preparation are typically time consuming, employing multistep procedures involving a high risk for loss of analytes and the use of extensive amounts of organic solvents. Moreover, the sampling step could give inadequate results due to possible loss of volatile substances during extraction. That is why today classical liquid-liquid extraction is replaced by elegant sorbent-based extraction methods, e.g. by Solid Phase Microextraction (SPME) (Pawliszyn, 1997; Tang and Isacsson 2008).

The release of soluble constituents upon contact with water is regarded as a main mechanism of release, which results in a potential risk to the environment during the reuse or disposal of waste materials (Twardowska, 2004). Consequently, determination of the amount of the mobile and bioavailable contaminants instead of the total amount of contaminants in the risk analysis of solid materials in utilization and deposit sites is very important (Yang et al., 2007; Roskam and Comans, 2009; Witt et al., 2009; van der Sloot and Kosson, 2012). Taking into account the substantial amounts of deposited waste and possible environmental impact the knowledge about the leaching behaviour of wastes and waste-based materials is crucial for proper waste management.

For the determination of leaching behaviour laboratory leaching standard methods are used. However, laboratory studies do not always relate directly to field conditions, and do not allow to completely assess the long-term release of contaminants, especially persistent pollutants from industrial waste deposits. Studies on field leaching under natural outdoor conditions are not very popular, as they remain to be difficult and expensive. The attempts to better understand the fate of pollutants using field leaching is complicated by a number of variables that have to be taken into account. However, to improve risk assessment of organic contaminants in wastes, the site-specific approach should be used, which takes into account any characteristics that influence actual local risks. Moreover, spent shale deposit can act as a model for understanding the long-range processes, which occur in industrial solid wastes.

When analyzing complex matrices, such as waste materials, containing organic matter and non-aqueous liquids it is very important to evaluate risks associated with bioavailability of hydrophobic contaminants (Kraaij et al., 2003; Enell et al., 2004; Kalbe et al., 2008). Although many studies have investigated the total dissolved concentration of PAHs in hazardous waste disposals, only a few studies have examined the freely dissolved concentration of PAHs in leachates

from contaminated solid matrices. Investigations indicated that the environmental impact of hydrophobic organic contaminants, e.g. PAHs is based on active/freely dissolved concentrations (C_{free}) rather than the total amounts, as C_{free} is responsible for sorption and uptake into macro- and micro-organisms (Van der Wal et al. 2004; Ter Laak et al., 2006; Witt et al., 2009). Determination of the bioavailable fraction of PAHs could be done by SPME method (Witt et al., 2009; Kraaij et al., 2003).

It is beneficial to find ways to increase the value of waste materials. In this approach a residue can be viewed as a by-product of the industrial process rather than waste. The use of waste-based products in the construction industry is considered to be a relatively safe method of reusing. One of the promising ways of reuse of oil shale ash is utilizing it in construction materials (Raado et al., 2014a). Utilizing oil shale ash in cement production reduces the need for raw materials and decreases the ash amounts deposited to ash fields and consequent environmental contamination. As oil shale processing wastes contain pollutants it is essential to assess which compounds and amounts could be released to the surrounding environment before using waste-based products on a large scale. Estonia has more than a fifty-year experience of using PF oil shale ash as a constituent of Portland cement, however CFB oil shale ash is a new material (Raado et al., 2014b). Leaching characteristics of products from abovementioned source materials are not equally well researched. Therefore, a comparative study of the ash-based materials originating from the new CFB combustion technology and the old PF is needed. As the relevant information on leaching behaviour from hardening oil shale waste-based construction materials is currently absent, this study aims to fill these data gaps. The leaching behaviour of waste-based materials is usually studied using predominately powder-like (or granular) material. However, the leaching behaviour of monolithic and powder-like (or granular) materials differs considerably, mostly because of the higher porosity and permeability of granular materials (Twardowska and Szczepanska, 2002; Tiruta-Barna et al., 2006; van der Sloot and Kosson, 2012; Garrabrants et al., 2014). Leaching of contaminants from granular materials occurs predominately through percolation of the product and for monoliths by diffusion through the surface. Although there limited data about waste containing monolithic products (i.e. from coal fly ash and municipal solid waste incinerator ash) exist, the data about leaching behaviour of oil shale ash monoliths are practically absent. It is, therefore, necessary to assess the waste-based materials leaching behaviour not only from granular waste-based products but also from monolithic types. Based on this information it is possible to characterize the hazard of the waste in site-specific conditions, transport, and long-term changes in the utilization/disposal conditions.

To summarize, the assessment of long-term influence of industrial wastes on the surrounding environment requires reliable data on the fate of organic and inorganic pollutants. The wastes concerned are the oil shale processing wastes from the oil shale industry in Estonia. In general, the environmental impact of the pollutants is related to their availability for transport and bio-uptake, rather

than their total concentrations in waste material. The purpose of the work was to investigate the long-term fate of PAHs and heavy metals in the environment from oil shale processing waste disposal at field conditions, with the special emphasis on hazardous PAHs. The monitoring of PAHs in complex environmental samples requires optimised sampling and analytical methods that assure reliable concentration measurements. New SPME method will be developed and optimised for the bioavailable fraction of PAHs determination. Although waste-containing materials may be technically suitable, it is important to understand their potential environmental impact before using waste-based products on a large scale. Comparative study of the ash-based materials originating from the new CFB combustion technology and the old PF is needed. It is of special interest to assess leaching characteristics from both granular and monolithic waste-based material.

2. AIMS OF THE STUDY

The main objective of this study are to evaluate environmental properties of oil shale processing solid wastes and waste-based materials. For this purpose, the leaching behaviour of organic and inorganic persistent pollutants, PAHs and metals presented in wastes, will be studied in field and laboratory conditions (Fig. 1).

The specific aims are:

1. The investigation of the long-term leaching behaviour of pollutants by monitoring both aged and fresh spent shale at actual field conditions.

2. The monitoring of PAHs requires optimised analytical methods that assure reliable concentration measurement. GC-MS method for analyzing of PAHs in spent shale leachates will be optimized, F-PAHs as internal standard will be tested.

3. Solid Phase Microextraction (SPME) method will be developed and applied for the analysis of bioavailable PAHs in spent shale leachates. The optimum range of conditions for the SPME extraction of PAHs and their quantification using GC/MS will be determined.

4. The total PAHs' concentration will be measured by traditional solvent extraction, and freely dissolved PAHs' concentrations will be measured by SPME technique in leachate samples from spent shale deposit. SPME method will be used to determine the bioavailable fraction of PAHs in deposited material in field conditions and to characterize the role of freely dissolved concentrations (C_{free}) of PAHs in leachates from the real waste disposal.

5. The actual leaching of selected elements from the fresh and aged spent shale deposit at field conditions will be evaluated. The metals will be selected due to their potential risk to the environment and human health.

6. The leaching of PAHs and metals from PF and CFB oil shale ash and ash-based construction materials will be studied. For evaluation of leaching behaviour of pollutants laboratory leaching tests will be used. The EN 12457-2(2002) batch leaching test for granulated matter and the EN CEN/TC 15862(2012) batch leach test providing information on the leaching of monolithic waste will be performed. Leaching data for the PAHs, selected metals as well as pH and electrical conductivity of ash and ash-based construction materials will be compared.

3. LITERATURE REVIEW

3.1. Oil shale processing solid wastes

Oil shale is considered to be the alternative to fossil energy resources such as petroleum and natural gas. In terms of world reserves, oil shales are seen to be second highest, after coals. Oil shales are widely distributed around the world: more than 600 deposits are known in more than 30 countries on all continents. Shale oil resources are almost 500 billion tonnes, or approximately 3.2 trillion barrels (EASAC, 2007). The biggest shale oil resources are known in USA, Brazil, Jordan and Morocco. Estonia is the only country in the world that operates oil shale fired power plants to supply most of its electricity to domestic customers and can export power to other countries. In addition to thermal power plants, Estonia has also oil shale thermal processing plants for shale oil production. More than 90 years of experience in oil shale processing make Estonia's oil shale industry the most developed in the world. Oil shale gained its leading role in the energy balance of Estonia before the Second World War and although total energy consumption has grown remarkably since that time, oil shale has remained the dominant fuel.

Oil shale is a sedimentary rock containing organic matter, kerogen, and belongs to the group of sapropel fuels (Ots, 2006). Estonian oil shale is characterized by high ash content (45–50%), low net calorific value (8–12 MJ/kg), moderate content of moisture (11–13%) and sulfur (1.4–1.8%). The dry matter in Estonian (kukersite) oil shale consists of three parts (wt.%): organic matter (ca 30%), carbonate components (ca 45%), and sandy-clay components (ca 25%). The chemical and mineralogical composition of all these separate components is quite constant, irrespective of the deposit location and layer (Arro et al., 2003). The main characteristics of the organic matter of oil shale are high hydrogen (9.7%) and oxygen (10%) content and low nitrogen percentage (0.33%). Oil shale organic matter contains on average about 1.8% of organic sulphur. An important characteristic of the organic matter is high chlorine content (0.8%). The mineral matter of oil shale can be divided into two large groups: sandy-clay or terrigenous part and carbonate matter. In an oil shale seam, organic matter is tightly bound with sandy-clay minerals and forms a uniform mixture (Ots, 2006). The main component of the oil shale carbonate matter is calcium oxide (48.1%), followed by magnesium oxide (6.6%). The main components in the sandy-clay part are SiO_2, Al_2O_3 and K_2O. The content of potassium (as K_2O) exceeds that of Na_2O by about 8 to 12 times (Ots, 2006). The mineral part oil shale contains a wide range of elements, which may be divided into two groups: major elements (Ca, Si, Al, Mg K, Fe, Na, S, P, Cl, Zn, Sr, Ti) and trace elements (e.g. As, Cd, Cr, Co, Cu, Hg, Mn, Ni, Sb, Tl, V, Mo, Sn, Ba, Pt, Rb, Th, U).

The two primary utilization pathways for oil shale are oil production by retorting and electricity generation by combustion of oil shale (Fig. 1). The majority (close to 90%) of mined oil shale is utilized in thermal plants for

electricity and heat production (Eesti Energia Annual Report, 2014). Due to high mineral content oil shale industry produces huge amounts of waste – spent shale from retorting and oil shale ash from combustion.
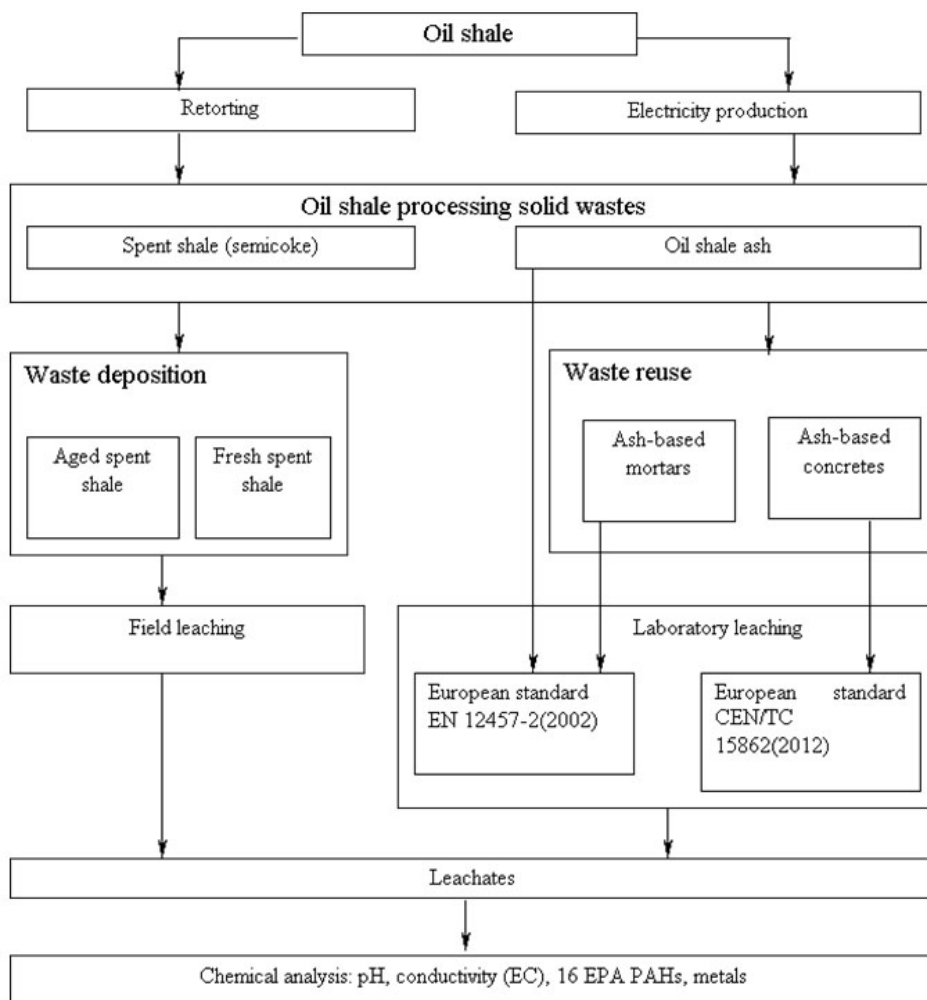
Figure 1. Scheme of the study of leaching behaviour of different oil shale processing solid wastes.

3.1.1. Spent shale as waste from retorting

A part of oil shale excavated in Estonia is used for thermal processing (semi-coking or retorting) to produce oil (Veiderma, 2003; Saether et al., 2004; Sedman et al., 2012). According to the World Energy Council, in 2005, more than half of the total shale oil in the world was produced in Estonia (Survey of Energy Resources, 2007). At present, two different oil shale retorting techno-

logies are employed in Estonia: the Kiviter-type internal combustion vertical retort and the Galoter type or solid heat carrier (SHC 140) unit (Veiderma, 2003). The Kiviter thermal processing of oil shale in Estonia started in 1924, the Galoter retorting process has been employed since 1980 (Veiderma, 2003). During retorting, oil shale is heated in the absence of oxygen to the temperature at which it is decomposed into oil, gas and solid residues. Due to the high content of mineral matter in oil shale a significant amount of spent shale (also called semi coke) is formed, which has been deposited close to the retorting plants. Three tonnes of wastes, with each tonne of commercial shale oil is produced under the technology in current use (Veski, 2005). More than 100 million tons of spent shale has been stored in piles since the beginning of oil production in 1921. Spent shale deposits consist of heterogeneous layers with variable properties and composition, which undergo mineralogical and chemical transformations along with alteration of its physical properties. Spent shale deposit sites are a major concern in oil shale industry, because of the volume of the disposed wastes and the potentially harmful compounds it contains.

The spent shale has been classified as hazardous waste in Estonia due to the high alkalinity. Spent shale is characterized by a considerable amount of organic compounds (7–24 mass percents). It also contains trace elements (it will be discussed further in Section 3.3). Toxic compounds like water-soluble phenols, PAHs as well as tarry and bituminous substances are found in spent shale (Orupõld et al., 2008; Otsa and Tang, 2003; Saether et al., 2004; Trikkel et al., 2004). Spent shale from the Kiviter and Galoter processes are different, due to different temperatures and other parameters used during retorting (Veiderma, 2003; Saether et al., 2004). The chemical composition of spent shale is also dependent on the composition of oil shale. Spent shale deposits consist of heterogeneous layers with variable properties and composition, which undergo mineralogical and chemical transformations along with alteration of its physical properties (Veiderma, 2003; Mõtlep et al., 2007; Sedman et al., 2012; Trikkel et al., 2004).

3.1.2. Oil shale ash – waste from combustion

The two most powerful Estonian Thermal Power Plants (Eesti and Balti) use two different oil shale combustion technologies: pulverized firing (PF) and circulating fluidized bed combustion (CFB) technologies. Until 2004, oil shale was industrially combusted in Estonia only by PF technology. Since 2004 new boilers based on CFB combustion technologies have been taken into service. CFB is one of several advanced approaches for substantially improving the efficiency, while significantly reducing emissions. Currently, 20 PF boilers and 4 CFB boilers operate at the Thermal Power Plants (Bityukova et al., 2010). Oil shale is burned directly in a combustion chamber. Oil shale ash is a silica-based powder with little to no volatile organics present. Ash content of the oil shale after burning is about 45% in the dry state (Bauert and Kattai, 1997). During the 1980s 10–11 million tons of oil shale ash was formed annually in four oil shale fired Power Plants (Eesti, Balti, Kohtla-Järve and Ahtme). At the beginning of

the 1990s, the amount of oil shale burnt and therefore the amount of ash formed decreased, and now it is on the annual level of 5–6 million tons. Oil shale ash has more reusability applications than spent shale from retorting plants. A part of the oil shale ash is used in the industry of construction materials, agriculture for liming acid soils or in road construction (Ots, 2006). However, most of the ash formed is wet deposited to the nearby ash fields. The ash fields near Power Plants are Estonia's largest waste handling sites and cover a total of 13 km^2. Total oil shale ash volume is about 300 Mt, which has created a severe problem and is to be solved in the future (Saether et al., 2004). The largest part of this solid waste is furnace ash. The finer and lighter ash particles (fly ash) collected in cyclones and electrostatic precipitators are also deposited in the ash fields.

The main environmental concern with respect to the disposal of oil shale ash is the formation of highly alkaline leachates (pH 12–13). In the Estonian registry of waste, the oil shale ash is registered as hazardous waste due to the high alkalinity of the leachates. The very alkaline leachates formed as a result of water filtration through the ash plateaus account for the contamination of environment around the ash fields.

The main difference between the two oil shale firing technologies is the combustion temperature in the furnace chamber and the method of combustion (Ots, 2006). In the PF boiler furnace the maximum combustion temperature can reach temperatures up to 1400–1500 °C, while in the CFB boilers the firing occurs at the lower temperature: 800–900 °C. The much lower combustion temperature and the enhanced phase separation in CFB units result in significantly different chemical, physical and phase composition of CFB ash compared to PF ash. The contents of the amorphous Al-Si glass phase in PF fractions varies significantly with the position in the ash removal system (1.1–37.8%) (Mõtlep et al., 2012). In the case of CFB ash, the content of the amorphous phase was found at about 10–15%, showing no significant variations between ash fractions (Kuusik et al., 2012; Pihu et al., 2012). Oil shale firing mode has influence to the shape of fine ash particles. Thanks to the higher combustion temperature PF ash is characterized by large portion of particles with regular spherical shape with smooth surface. Particles of CFB ashes are characterized by irregular shape as well as by porous and uneven surface (Kuusik et al., 2005; Reinik et al., 2007; Bityukova et al., 2010). The surface area of the PF ash samples collected at the first unit of electrostatic precipitator is 0.5 m^2/g and 6.9 m^2/g for the CFB ash according to Reinik et al. (2007) study.

3.2. PAHs in oil shale processing solid wastes

3.2.1. Distribution of PAHs

Spent shale contains complex mixture of organic and inorganic compounds. Spent shale and their utilization products could be the source of pollution, as contain organic (polycyclic aromatic hydrocarbons – PAHs) and inorganic (heavy metals) pollutants. For simplification of the analysis and regulation purposes the US Environmental Protection Agency (EPA) has made a list of 16 unsubstituted PAHs that are on a priority pollutant list. These PAHs are usually referred to as the EPA 16 PAHs (Table 1) and are the PAHs most commonly analyzed for. They are also included to priority hazardous substances by the EC (Regulation EC No 166/2006).

Table 1. Selected physical properties of the EPA 16 priority PAHs (Nollet, 2006; Mackay et al., 2006).

Polycyclic aromatic hydrocarbons	Abbreviation	Molecular weight, g/mol	Water solubility, mg/l	Log K_{oc}*	Log K_{ow}**
Naphthalene	NA	128	31	3.11	3.37
Acenaphthylene	ACN	152	16.1	3.83	4.0
Acenaphthene	AC	154	3.8	3.79	3.92
Fluorene	FL	166	1.9	4.15	4.18
Phenanthrene	PHE	178	1.1	4.22	4.57
Anthracene	AN	178	0.045	4.41	4.54
Fluoranthene	FA	202	0.26	4.74	5.22
Pyrene	PY	202	0.132	4.82	5.18
Benzo[a]anthracene	B[a]A	228	0.011	5.66	5.91
Chrysene	CHR	228	0.002	5.37	5.75
Benzo[b]fluoranthene	B[b]F	252	0.0015	5.89	5.8
Benzo[k]fluoranthene	B[k]F	252	0.0008	5.89	5.8
Benzo[a]pyrene	B[a]P	252	0.0038	5.71	6.04
Indeno[1,2,3cd]pyrene	IP	276	0.00019	6.14	6.58
Dibenz[a,h]anthracene	D[a,h]A	276	0.0005	5.97	6.75
Benzo[g,h,i]perylene	B[g,h,i]P	278	0.00026		6.50

* K_{oc} organic carbon partition coefficient
** K_{ow} octanol-water partition coefficient

The content of PAHs in the spent shale could be more than 13 mg/kg (Otsa and Tang, 2003; Saether et al., 2004; Kirso et al., 2007). Its distribution in solid matter is presented in Table 2 (Otsa and Tang, 2003). The total content of PAHs in fresh material has been estimated 13.34 mg/kg, and in aged spent shale 13.29 mg/kg, very close to that of the fresh material. In other words, the profile and content of the individual PAHs was not changed even after 10 years of storage indicating their general persistence in the environment. A typical petrogenic

PAHs profile includes mainly alkylated homologues, and the parent PAHs are least abundant compared to the substituted ones. According to previous studies (Havenga et al., 1999), alkylated naphthalenes make up approximately 99% of the total amount, and parent compounds only 1%. For phenanthrenes the corresponding ratio was found to be 88% and 12%, respectively (Havenga et al., 1999). Thus, the total content of PAHs in spent shale wastes may be significantly higher if substituted derivatives are taken into account.

Table 2. Content of PAHs (mg/kg) in aged and fresh spent shale samples (Otsa and Tang, 2003).

PAHs	Aged spent shale	Fresh spent shale
NA	1.75	1.53
ACN	0.12	0.12
AC	0.23	0.27
FL	0.14	0.31
PHE	1.13	0.96
AN	0.55	0.67
FA	0.58	0.37
PY	1.2	1.2
B[a]A + xylene	1.02	1.04
B[b]F+B[k]F	0.47	0.31
B[a]P	0.81	0.85
B[g,h,i]P	0.6	0.54
IP	0.33	0.25
Sum of PAHs	13.29	13.34

As shown in the study (Kirso et al., 2005, Table 3), the total concentration of 16 EPA PAHs in the oil shale ash fractions from electrical precipitators in the Estonian Power Plant was found to be in the range of 82.2–152.1 µg/kg for the PF process, whereas for the new CFB technology, the total content of PAHs was lower, resulting in 30.2–63.7 µg/kg. Priority PAHs' concentration at CFB oil shale ash was much lower than at PF oil shale ash. As previously mentioned, FBC and PF technologies operate at different combustion temperature (800–900 °C against 1400–1500 °C, respectively). It leads to formation of oil shale ash with different properties (see Section 3.1.2.) and also to different concentration of PAHs in the ashes (Table 3).

Table 3. Range of concentrations (µg/kg) of 16 EPA PAHs in PF ash and CFB ash fractions of electrostatic precipitators (Estonian Power Plant, Estonia) (Kirso et al. 2005).

PAHs	PF ash	CFB ash
NA	7.1 – 13.0	2.5 – 5.0
AC	2.0 – 3.2	1.3 – 2.1
ACN	nd*	nd
FL	2.1 – 4.1	1.2 – 2.2
PHE	4.0 – 7.4	2.1 – 4.0
AN	3.6 – 7.5	1.2 – 3.1
FA	5.3 – 9.3	2.1 – 4.1
PY	5.9 – 11.0	2.0 – 4.5
B[a]A	6.5 – 12.0	2.3 – 5.0
CHR	8.5 – 15.1	2.7 – 6.8
B[b]F	6.6 – 12.4	2.3 – 5.1
B[k]F	0	0
B[a]P	7.9 – 15.1	2.8 – 6.4
D[a,h]A	7.3 – 13.5	2.5 – 5.6
B[g,h,i]P	8.9 – 16.2	2.9 – 6.5
IP	6.8 – 12.2	2.3 – 5.0
Total	89.0 – 152.1	30.2 – 63.7

* nd – not detected

3.2.2. PAHs properties

PAHs are ubiquitous environmental contaminants derived from the incomplete combustion of organic materials such as gasoline, wood, coal or oil shale; they are also formed during food preparation (barbecuing, smoking). Even if there are some natural sources, PAHs originate mostly from anthropogenic activities based on fossil fuel and organic matter incomplete combustion. PAHs is a specific group of organic pollutants, which include a wide range of compounds: carbo-cyclic and heterocyclic, substituted and non-substituted homologues. PAHs can persist, transport and accumulate in the environment to the extent that the potential for adverse environmental effects is considerable (Alexander, 1995; Enell et al., 2004). Their presence in the environment is highly undesirable because of the carcinogenic and mutagenic properties of many representatives of this group of compounds. Generally, PAHs are characterized as very hydrophobic (lipophilic) organic compounds and therefore they are present in aqueous phase on trace level (Bjorseth and Ramhal, 1985; Mackay et al., 2006). They have a high affinity for organic matter, and when present in waste, soil or sediments they tend to remain bound to solid particles (Roskam and Comans, 2009). As a rule, water solubility of PAHs is decreasing and hydrophobic character is increasing with increasing molecule size (number of rings) (Table 1). These characteristics affect the dispersion of PAHs in the solid matrices.

Fate of PAHs in the environment are determined to a large extent by physicochemical properties such as water solubility, vapor pressure, Henry's law constant, octanol-water partition coefficient (K_{ow}), and organic carbon parti-

tion coefficient (K_{oc}) (Bjorseth and Ramhal, 1985; Harvey, 1998; Nollet, 2006). Some of the transport and partitioning characteristics (e.g. Log K_{oc} values and Log K_{ow} values, Table 1) of the 16 EPA PAHs are roughly correlated to their molecular weights. They are often discussed in the literature by grouping these PAHs as follows: low molecular weight compounds (152–178 g/mol) – AC, ACN, AN, FL, and PHN (for abbreviations see Table 1); medium molecular weight compounds (202 g/mol) – FA and PY; and high molecular weight compounds (228–278 g/mol) – B[a]A, B[b]F, B[k]F, B[g,h,i]P, B[a]P, CHR, D[a,h]A, and IP (ATSDR, 1995). On the basis of properties PAHs can be also distinguished to two- and three-ring and four- to six-ring compounds.

Deposits of oil shale processing wastes may be detrimental to the environment as well as to human health because of mobilization of PAHs. Therefore the long-term fate of PAHs in the environment represents a subject of interest.

3.2.3. Bioavailability of PAHs

Many investigations indicated that the environmental impact of hydrophobic organic contaminants in aquatic systems, e.g. PAHs is based on freely dissolved concentrations (C_{free}) rather than the total amounts, as freely dissolved fraction is responsible for sorption and uptake into macro- and micro-organisms (Poster et al., 2006; Kalbe et al., 2008; Van Der Wal et al., 2004). "Freely-dissolved" refers to the concentration in the water not associated with colloids or dissolved organic matter (DOM), and which thereby is readily available to the microorganisms (Fauser and Thomsen, 2002; Durjava et al., 2007). In other words bioavailability of hydrophobic organic contaminants is related to their freely dissolved concentration in water (Mayer et al., 2003; Ter Laak et al., 2006; Witt et al., 2009). Fate and bioavailability of very hydrophobic organic chemicals in aquatic ecosystems are affected by the presence of dissolved and particulate organic matter (Schwarzenbach et al., 2003).

The determination of freely dissolved (bioavailable) fraction of PAHs represents an analytical challenge due to ultralow aqueous solubility and incomplete phase separation of this fraction from competing phases in natural systems (e.g. mineral matter in wastes). A number of techniques are available for C_{free} measuring including equilibrium dialysis, ultrafiltration, ultracentrifugation, chromatographic methods, techniques based on passive partitioning in semi-permeable membrane devices etc. (Heringa and Hermens, 2003; Witt et al., 2009). One of the most promising techniques is Solid Phase Microextraction (SPME) introduced by Pawliszyn on 1997. SPME can measure only free or easily extractable/available fraction of the contaminants that is detected and analyzed by sampling with SPME fiber (Witt el., 2009; Kraaij et al. 2003). The concentration of compound in the fiber coating is directly related to the free concentration in the sample through the partition coefficient (K_{SPME}) of the chemical between water and chemical or by calibration curve established in water at fixed exposure time of the SPME fiber (Heringa and Hermens, 2003). Deter-

mination of the PAHs in the fiber after the extraction can provide information on C_{free} of a compound in the sample (Heringa and Hermens, 2003; Witt et al., 2009). Further, the combination of SPME with GC-MS could be applied for the extraction and quantification of PAHs in environmental samples (Akkanen and Kukkonen, 2003; Vas and Vekey, 2004; Hawthorne et al., 2005; Ouyang and Pawliszyn, 2006; Fernandez-Gonzalez et al., 2007). Even more, SPME was successfully used for estimation of bioavailable fraction of PAHs in different contaminated matrices, i.e. wastewater, soil, sediments (Van der Wal et al., 2004; Ter Laak et al., 2006; Cornelissen et al., 2009; Gomes et al., 2009; Witt et al., 2009).

3.2.4. Methods of PAHs determination

The determination of PAHs requires optimized sampling and analytical methods that assure reliable concentration measurements. The considerable variability of physico-chemical properties of PAHs and trace concentration of PAHs in different matrices make sampling, sample preparation and analysis especially challenging (Bjorseth and Ramhal, 1985; Harvey, 1998; Nollet, 2006). The determination of PAHs in water, soil and solid waste typically includes a separation step with subsequent cleanup and concentration of the sample, followed by final determination (e.g. with gas chromatography (GC) and mass spectrometry (MS) using electron-impact ionization).

Sampling preparation step is a key step in analytical process, as it is necessary to isolate the components of interest from a sample matrix since most analytical instruments cannot handle the matrix directly. Sample preparation includes extraction, concentration and cleanup. Sample preparation typically account for 30% of the errors encountered in the performance of analytical methods (Twardowska et al., 2004). Most authors recognize the need for some sample pre-treatment in order to simplify the sample matrix or reduce the amount of solvent when a solvent extraction is required. It is stated that the main source of low quality of analytical data is often the sampling, pretreatment, and separation of compounds and not the final step, i.e. quantification of PAHs. Moreover, the sampling preparation step could give inadequate results due to possible loss of volatile substances during extraction. A well-known classical method for separation of any group of organic pollutants from solid material is Soxhlet extraction (Nollet, 2006). Other extraction procedures/ techniques have been established in order to reduce the volume of extraction solvents and extraction times and improve the precision of recoveries. Such techniques include: focused microwave-assisted Soxhlet extraction or microwave-assisted extration; supercritical fluid extraction; accelerated solvent extraction has obtained a plenty of names and acronyms, i.e. pressurized solvent extraction, pressurized fluid extraction, enhanced solvent extraction; ultrasonic extraction; pressurized-liquid extraction (Ramsey et al., 1992; Shimmo et al., 2002; Wang et al., 2007; Nollet, 2006).

The classical methods of sample preparation employ multistep procedures and thus, typically time consuming, involving a high risk for loss of PAHs and the use of extensive amounts of organic solvents. SPME is alternative method to the traditional methods of sample preparation as it integrates solventless extraction, concentration and sample introduction in a simple process, by using a polymer-coated fibre (Doong et al., 2000; King et al., 2004; Zuazagoitia et al., 2007). It also minimizes disturbance of sample matrices. The main advantages of SPME compared to solvent extraction are the reduction in solvent use, the combination of extraction and analysis into one step, and the ability to examine smaller sample sizes. It can also provide high sensitivity and can be used for polar and nonpolar compounds in a wide range of matrices with direct injection to both the gas chromatograph and the liquid chromatograph. SPME aims at measuring trace concentrations within environmental matrices that always will contain interfering substances. This calls for a selective extraction, a selective chromatographic separation, and a specific detection. In analysis of PAHs in complex matrixes, like wastes, obtaining sufficient concentration of chemical in leachate can be problematic. SPME method is able to quantify very low (ng/l) concentrations of PAHs. So, SPME seems to be a promising sample-preparation method for PAHs, and may be used for quantitative determination as well as for the assessment of bioavailability of PAHs (Cam et al., 2004, Paper II).

Further, the combination of SPME with gas chromatography mass spectrometry (GC–MS) could be applied for the extraction and quantification of PAHs in environmental samples (Akkanen and Kukkonen, 2003; Vas and Vekey, 2004; Hawthorne et al., 2005, Quyang and Pawliszyn 2006; Fernandez-Gonzalez et al., 2007).

3.3. Metals in oil shale processing solid wastes

Raw kukersite oil shale includes a number of trace elements as As, B, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sn, Sb, Se, V and Zn (Häsanen et al., 1997; Saether et al., 2004). Heavy metals are considered a major anthropogenic contaminant in the environment worldwide. They pose a serious threat to human health, living organisms and natural ecosystems because of their toxicity, persistence and bio-accumulation characteristics (Bayen, 2012). Many heavy metal ions are known to be toxic or carcinogenic to humans (Arora et al., 2008; Bayen, 2012). The long-term accumulation of heavy metals in the environment is a concern because they potentially have significant consequences for the quality of the human food chain, toxicity to plants and soil microbial processes and once applied they have very long residence times in the environment. Trace elements are present at elevated concentrations at National Priority Lists. Environmental legislation in some countries (notably Germany and USA) gives limits on the leachability of certain trace elements. Metals can be transported by colloids or in dissolved forms depending on the metal concerned (Citeau et al., 2003; Zhao et al., 2009). However, little is known about the role of inorganic colloids in the

transport of metals from spent shale deposit into the surrounding environment (Pédrot et al., 2008).

Data for selected metals in raw oil shale and spent shale obtained from literature and determined in the Paper III are presented in Table 4. Contents of selected elements in ash samples of PF and CFB boilers from Estonian Power Plants reported in the literature are presented in Table 5. Data for trace element contents in oil shale ash from PF boilers has been presented in several studies (Häsanen et al., 1997; Aunela-Tapola et al., 1998; Blinova et al. 2012). Among these data we failed to find values for Sr, Sn and Rb and the radioactive elements U and Th in oil shale ash from Power Plants. Lack of information is clearly noticeable in the case of the lately introduced CFB boiler where only some traces were reported (Blinova et al., 2012). Depending on furnace temperature and residence time as well as the specific surface area of ash heavy metals in solid fuel may remain in the solid phase, or volatilize and then be carried in the flue gas along the gas duct or precipitate on ash particles. According to their behaviour in high-temperature combustion heavy metals may be divided in easily volatile (Hg, Sb, Rb, Zn, Cd, Pb), moderately volatile (Ba, Co, Tl, Sn, Ni) and hardly volatile (Cr, U, Th, V, Mo) elements (Ots, 2006). All toxic heavy metals are presented in oil shale ash in some given chemical compound, which can be assessed theoretically according to minimum value of Gibbs free energy for the system (Aunela-Tapola et al., 1998). For example, mercury is present in $HgCl_2$ at a temperature below 527 °C and at temperatures above 577 °C exist mainly as mercury vapor. The main lead compound at temperatures below 827 °C is $PbCl_4$ (g), at temperatures between 927 and 1027 $PbCl_2$ (g) and above 1027°C PbO (g) becomes predominant. The stabile cadmium compound below 327 °C is $CdCl_2$ (s), up to 877 °C the same compound is presented in gaseous phase. Above 877 °C, Cd is stable as metal in gaseous phase, while a small amount can also be present as CdO (g) (Ots, 2006). In addition to temperature the actual metal compounds and their phases may also depend on other process variables such as content of chloride in the solid fuel and other reactants in the system. Because of differences in combustion temperature and technology the behaviour of the selected heavy metals can differ between the PF and CFB boiler systems.

Table 4. Concentrations of selected metals (mg/kg) in raw oil shale, fresh and aged spent shale samples.

Element	Raw oil shale [*]	Fresh spent shale [*]	Fresh spent shale [**]	Rel SD, %	Aged spent shale [**]	Rel SD, %
Ca	159 000	168 000	217 100	3	296 300	0.4
Fe	18 500	55 650	24 000	3	35 000	2
K	8 500	44 556	6 160	0.2	6 500	2
Mn	214	385	340	3	458	2
Ba	45	nd	80	3	125	2
Zn	27	37	17	3	29	1
V	19	34	26	5	39	1
Pb	19	42	41	3	69	1
Cr	15	43	24	5	34	1
Ni	13	23	20	4	30	0.2
Cu	6	11	19	3	43	0.1
Mo	3	5	2	3	3	2
Co	2.6	nd[***]	3.4	3	5.2	3
Sb	0.3	nd	nd		nd	
Cd	0.2	0.1	0.1	6	0.1	5
Tl	nd	nd	0.3	2	0.5	1

[*] Saether et al., 2004
[**] Paper III
[***] nd – not determined

Table 5. Content (mg/kg) of selected metals in the ashes of oil shale fueled PF and CFB boilers of Estonian and Baltic Power Plants reported in the literature (Paper V).

Estonian Power Plant's PF boiler (Aunela-Tapola et al., 1998)

Ash fraction	Zn	Sr	Cd	Hg	As	Cr	Ni	Pb	Tl	Sb	Co	Cu	Mn	V	Mo	Ba
Bottom ash	96	–	<0.3	–	16	19	27	24	<0.1	<0.4	4.5	9.9	700	33	–	–
Super-heater	101	–	<0.4	–	18	23	29	44	<0.2	<0.8	4.9	11	700	40	–	–
Pre-heater	92	–	<0.3	–	14	19	26	34	<0.02	<0.6	4.5	9.5	690	35	–	–
Cyclone	93	–	<0.3	–	16	21	26	45	0.3	0.6	4.5	9.3	650	38	–	–
ESP* I and II	160	–	<0.8	–	42	33	31	130	1.3	0.9	5.3	9.6	470	52	–	–
ESP III and IV	310	–	1.8	–	59	49	38	210	2.3	1.1	6.6	12	440	73	–	–

Baltic Power Plant's PF boiler

Ref.	Zn	Sr	Cd	Hg	As	Cr	Ni	Pb	Tl	Sb	Co	Cu	Mn	V	Mo	Ba
Cyclone	Häsanen et al., 1997	51	–	0.2	–	10	26	26	32	–	0.4	5	16	493	43	4	147
ESP IV	Blinova et al., 2012	46	–	0.3	–	28	42	–	113	–	–	–	12	–	–	–	–

Baltic Power Plant's CFB boiler

Ref.	Zn	Sr	Cd	Hg	As	Cr	Ni	Pb	Tl	Sb	Co	Cu	Mn	V	Mo	Ba
ESP IV	Blinova et al., 2012	62	–	0.2	–	17	49	–	75	–	–	–	15	–	–	–	–

– no data
* ESP – electrostatic precipitator

3.4. Field leaching

Environmental risk of solid wastes is often evaluated on the basis of total concentration of pollutants. However, the environmental risk on the ecosystem is not only related to the absolute content of various potentially toxic elements and compounds in the solid waste. It depends on the mobility of pollutant when the residue comes in contact with water. It is almost impossible to assess the aqueous leaching behaviour from solid concentrations (Twardowska, 2004; Susset and Grathwohl, 2011). Thus, the evaluation of the leaching behaviour is an important aspect in waste management for the long-term protection of the environment. Although contaminants of concern are present at low content in spent shale, the large quantities of solid wastes aggregate huge amount of emissions entering the environment.

Fate of the non-degradable mobile elements and persistent organic pollutants is a matter of concern from the viewpoint of pollution and sustainability. The leaching of soluble constituents upon contact with water is regarded as a main mechanism of pollutants' release from the solid materials, which results in a potential risk to the environment (Twardowska and Szczepanska, 2002). In a waste deposit, the interactions between water and waste constituents lead to generation of leachates. Leachate is the largest long-lasting emission from deposited solid matter containing hazardous ingredients. Characteristics of wastes as well as hydrological, geochemical and biological processes may influence the fate and transport of pollutants in the disposal site (Van der Sloot et al., 1996; Orupõld et al., 2012; Sedman et al., 2012). The effect of spent shale disposal sites on the surrounding environment is an important consideration in both the short- and long-term view. Leachates from aged and fresh deposit can be used for the long-term study of inorganic and organic pollutants' fate in the environment.

The laboratory leaching tests are used to yield information on environmental properties of solid wastes. However, the laboratory leaching tests that are used may be a poor predictor of what happens in real life. Environmental risks can be over- or underestimated by the laboratory leaching tests (Kirso et al., 2007). In view of environmental impact, this may be a significant problem when the leachability is much higher or lower than predicted by leaching tests. Data on the process of leaching in field conditions from waste disposal sites are sparse due to the practical difficulties and expenses involved in the full-scale monitoring of sites and surrounding aquifers (Conell and Bell, 1992; Kirso et al., 2007; Haynes, 2009). Many studies have pointed out the importance of determining the mobility and bioavailability of contaminants in the risk analysis of solid materials both in utilization and deposit sites (Yang et al., 2007; Roskam and Comans, 2009; Witt et al., 2009; van der Sloot and Kosson, 2012). It is reasonable to assume that the more similar the test is to the full-scale situation, the more relevant the results of the test will be to real emissions from polluted soils or landfills (Kirso et al., 2007). Altered spent shale deposit sites characterized by relatively soft upper layer with thickness range 20–30 cm and

solid compacted matter in dipper layers (Mõtlep et al., 2007). Analysis of field leachates from the uppermost layer of the waste deposit may give reliable data to adequately evaluate the environmental impact of the deposition site. For this purpose a low-cost field leachate sampling method can be applied, which consists in collecting the infiltrate under gravity flow without disturbing the surface structure of the solid waste. Similar technique could also be used to investigate the behaviour of pollutants in the other types of waste deposition sites (Kirso et al., 2007; Mõtlep et al., 2007).

3.5. Leaching from waste-based materials

It is beneficial to find ways to increase the value of waste materials. In this approach a residue can be viewed as a by-product of the industrial process rather than waste. Utilizing of oil shale ash reduces the need for raw materials and also decreases the ash amounts deposited to ash fields and consequent environmental contamination. Besides reducing deposition of waste it also helps to economize on natural resources by reducing the need for raw materials. However, only minor amount of oil shale processing wastes are reused. Oil shale ash could be used as raw material in different applications, e.g. construction materials, agriculture, road building, carbonaceous fillers for pulp, paper plastics and rubber industry, also oil shale ash can be used for CO_2 elimination from flue gases (Kuusik et al., 2005; Kuusik et al., 2009; Velts et al., 2009; Uibu et al., 2009; Adamson, et al., 2010; Kõiv et al., 2010; Reinik et al., 2011; Raado et al., 2011; Pihu et al., 2012). Oil shale ash can also be used in stabilization/solidification for immobilizing contaminants of potential concern prior to storage (Raado et al., 2011; Catalan et al., 2011). It also has unique content of free lime and secondary clinker minerals and can be effectively used as secondary material for construction purposes (Bityukova et al., 2010; Kuusik et al., 2012; Raado et al., 2014a; Raado et al., 2014b). The PF ash has been effectively used as a second main constituent of Portland since 1960. Further utilization of the low-temperature CFB ash depends on its composition and properties. The use of cement-based solidification/stabilization products in the building industry is considered to be relatively safe method of reusing.

Although waste-containing materials may be technically suitable, it is important to understand their potential environmental impact before using ash-based products on a large scale. In recent years due to the increase of the utilization of combustion ash more attention is paid to environmental regulations of waste and waste containing materials. The leaching behaviour of waste and construction material based on waste is influenced by the chemical nature of the material, the nature of the leachant, the contact time of the leachant with waste and release mechanism (solubility or diffusion) (Tiruta-Barna et al., 2006; Enell et al., 2008; van der Sloot and Kosson, 2012; Butera et al., 2014). The leaching behaviour of monolithic and granular (or powder-like) materials differ considerably mostly due to higher porosity and permeability of the granular

materials. Leaching processes in granular materials take place predominately in the pores but in monolithic materials through the surface of the monolith. It has been revealed that the controlling mechanisms of the release are the equilibrium and mass-transfer based ones for granular and monolithic materials, respectively (van der Sloot and Kosson, 2003). As leaching behaviour of contaminants from granular and monolithic materials is different, separate tests have to be conducted for them.

The leaching behaviour of combustion residues including oil shale ash (Paper VI; Laja et al., 2005; Urb et al., 2007) and other fly ashes is studied using predominately powder-like materials (Shi and Kan, 2009; Izquerdo et al., 2012; Jones et al., 2012; Rocca et al., 2012; Tsiridis et al., 2012). PF ash is used as constituent in Portland cement for the long time, however, CFB ash is a relatively new material, and consequently leaching characteristics of products from above-mentioned source materials are not equally well researched. Although limited data about waste containing monolithic products i.e. from coal fly ash (van der Sloot et al., 2012) and municipal solid waste incinerator ash (Van Gerven et al., 2004; Van der Sloot et al., 2007; Galiano et al., 2011) exist, the data about leaching behaviour of oil shale ash monoliths are practically absent.

4. EXPERIMENTAL

4.1. Field leaching

4.1.1. Study site

The studied waste deposit is located at Kohtla-Järve (Northeast Estonia) close to an oil shale retorting plant (Viru Keemia Grupp). Leachate water samples were taken from both the closed part of the deposit (aged waste, A) and from the active part of the site currently in use (fresh waste, F) (Figs. 1, 2). The distance between the active and closed sites was approximately 200 m. The sampling points in the closed deposition site were situated at a 10–30º slope triangularly at 3–5 m distance from each other. In the fresh spent shale deposition site the sampling area was flat and samplers were placed on a 10 m² area. Five sampling points were situated in the aged and three in the fresh waste of the deposit (Fig. 2). Leachate water samples were collected during 2004–2010.
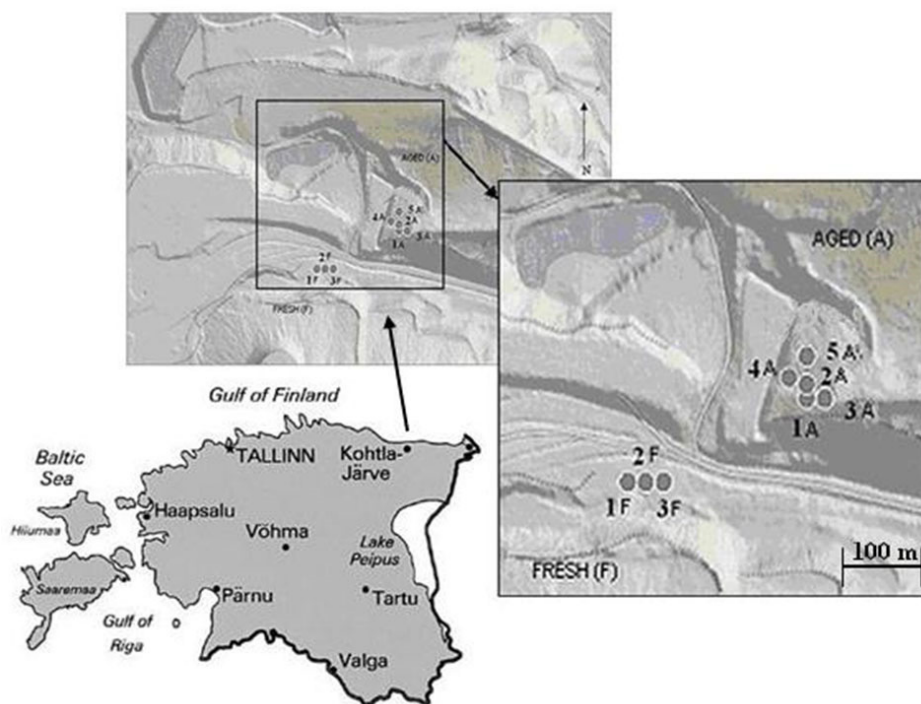

Figure 2. Location of the sampling points in spent shale deposit.

4.1.2. Sample collection

Sampling devices made from stainless steel (with dimensions 24.5×21.5 cm) was used for collecting leachate samples (for more information, see Kirso et al., 2007; Paper III). Samplers were installed by excavating a pit into the spent shale massive and pressing the sampler into the bank 15–20 cm below the surface, leaving soil beneath undisturbed (Fig. 3). Plastic containers (1L) were placed in the excavated pit and connected to the sampler by a PTFE pipe. Sampling points in the aged waste deposit site were situated on a 10–30° slope whereas the sampling from the fresh waste deposit was done in a flat area. The water collected by the end of the period was analyzed. Volume of collected liquid samples varied significantly during the test period (from absolutely dry bottles to full one-liter sample bottles). Unfiltered leachate samples were used for PAHs concentration measurement.

Figure 3. Installation of a sampler at the closed site of the spent shale deposit.

4.1.3. Climate data

Meteorological conditions were obtained from Estonian Institute of Meteorology and Hydrology (EIMH) from the nearest meteorological station in Jõhvi ca 10 km from the study field. The monthly average precipitation and monthly average temperature values recorded are presented in Fig. 4.
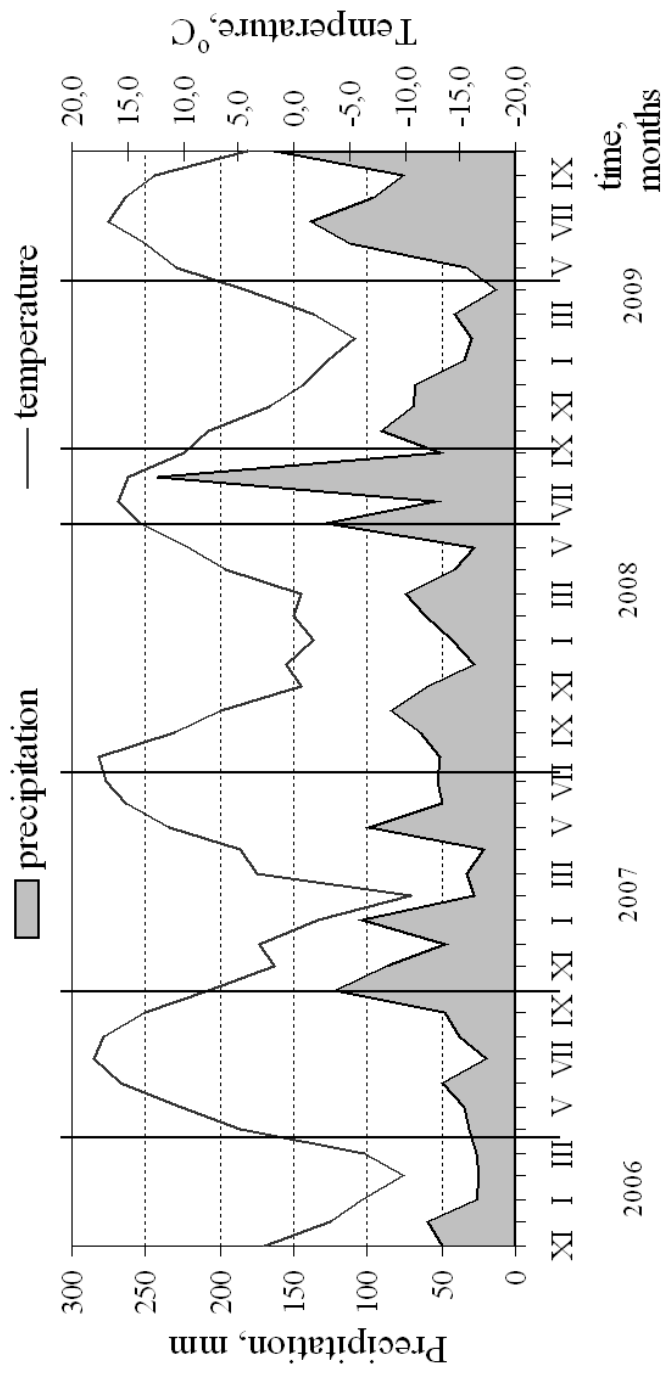
Figure 4. Sample collection periods (vertical lines), monthly average precipitation and temperature data recorded at Jõhvi weather station, EIMH in 2005–2009.

4.2. Laboratory leaching tests

A scheme on the assays of leaching behaviour of PAHs in oil shale ash and oil shale ash – based mortars and concrete is shown in Fig. 1, details of the experimental procedures are described below.

For chemical characterization of combustion by-products and waste materials, the so-called shake test is commonly used, that is, European standard EN 12457(2002), Characterization of Waste–Leaching–Compliance Test for Leaching of Granular Waste Materials and Sludges, according to the Council Decision 2003/33/EC (Paper VII; Paper VI; Kirso et al. 2007; Barbosa et al. 2011; Stiernström et al. 2011; Stiernström et al. 2014). Oil shale ash samples and oil shale ash – based mortar samples were subjected to EN 12457-2(2002) leaching test (see Fig. 1). The test provides information on the leaching of soluble constituents upon contact with water under the experimental conditions. The test was performed with two subsequent extraction cycles of the same portion of material with a fresh amount of water. The water extracts (leachates) were then used for further chemical analysis. The following procedure was applied: each sample (60 g) was leached with deionised water (liquid/solid ratio 10 L/kg) during 24 hours at room temperature (20 °C). Milli-Q water purification system (Millipore SAS, France) was used to produce deionised water. At the end of extraction the suspensions were separated by a vacuum filtration system equipped with a water aspirator pump, a 1-L filter flask, a Büchner funnel and a disposable 0.45-µm PA membrane filter (HIMIFIL, Estonia). The leaching/filtration procedure was performed in duplicate for each type of sample. The water extracts (leachates) were used for further chemical analysis.

Oil shale ash-based concrete samples were subjected to leaching test by EN CEN/TC 15862(2012) (see Fig. 1) at a specified liquid to surface area ratio (L/A) of 12 (cm^3/cm^2). Leaching tests were performed with concrete specimens with different hardening time: 7, 28 and 91 days. Specimens with dimensions 10x10x10 cm were leached using deionised water at room temperature 20°C for 24 hour in two parallels (Fig. 5). A block of concrete was placed on a covered glass dish and deionised water was added. The leaching takes place only from the specimen surface that was in contact with water. All glassware was cleaned before use and flushed with demineralized water followed by deionised water. After the leaching procedure, eluates were separated and pH and electrical conductivity were measured after which the eluates were used for additional analysis.

Figure 5. Tank leaching test for oil shale ash-based monoliths at National Institute of Chemical Physics and Biophysics in 2013.

4.2.1. Mortar and concrete samples

Three high-temperature PF ash samples and two low-temperature CFB ash samples from the Estonian Power Plant were used for making mortar and concrete samples. Descriptions of the samples are given in Table 6. Mortar and concrete samples with 7, 28, 91 days of hardening was made and characterized at Tallinn University of Technology. The treatment procedures are presented in Raado et al. 2014a, Raado et al. 2014b, Paper VIII.

Table 6. Characterization of oil shale ash samples (Estonian Power Plant, Estonia).

Sample	Description	Boiler
PF/1A EF1-3	Ash from the 1st to 3rd fields of electrostatic precipitators (ESPs)	PF
PF/1A EF1	Ash from the 1st field of the electrostatic precipitator (ESP)	PF
PF/1A CA	Cyclone ash	PF
CFB/8A EF1	Ash from the 1st field of the ESP	CFB
CFB/8Amix	Ash mixture from separation systems	CFB

Mortar samples containing either PF ash or CFB ash were made by mixing a binder with sand at a 1:3 weight ratio, using water until they were of equal consistency (Raado et al. 2014a). Mortars with dimensions of $40 \times 40 \times 160$ mm^3 were hardened in moulds for 48 ± 2 h and then 5 days at 20 ± 2 °C and a relative humidity $65 \pm 5\%$. The specimens were then further hardened at 20 ± 2 °C and

95 ± 5% relative humidity until testing. After 7, 28 and 91 days of hardening, the mortars were prepared for the testing of their leaching properties by crushing and sieving them through a 1 mm mesh.

Concrete samples were prepared by mixing ash, limestone aggregates and water (Raado et al. 2014b). PF and CFB ash samples were used (for more information see also Paper VIII). Mixing occurred in the laboratorial concrete mixer, into which the components were added in the respective order of filler, ash and water. For the preparation and hardening (curing) of concrete samples, the standard EVS-EN 123902:2009 was used with minor modifications. All samples were prepared using an ash-to-filler ratio of 1:1. Water was added in a quantity that would provide samples with similar qualities of workability. The concrete mixture was kept in the moulds ($10{\times}10{\times}10$ cm^3) for 48 h. After 48 h, specimens were extracted from the moulds and placed under the conditions of 95 ± 5% relative humidity and 20 ± 2 ℃ to harden them until further experimental work. Concrete samples were obtained with hardening times of 7, 28 and 91 days.

4.3. Leachate characterization

General characteristics (pH and conductivity) of leachates were measured using a BENCH PC 510 pH/Conductivity Meter (Eutech Instruments Pte Ltd, Singapore/Oakland Instruments, Vernon Hills, IL, USA). The electrode was calibrated with pH buffer solutions before each determination. Blank tests without sample but applying the same procedure were carried out in parallel for each set of analyses.

4.4. Chemicals

The 16 EPA's priority PAHs studied in the present work are listed in Table 1. A standard mixture of 16 PAHs at a concentration of 100 μg/ml in toluene were purchased from Chiron AS (Trondheim, Norway). Solvent n-hexane (analytical grade) was obtained from Merck (Darmstadt, Germany), and deionised water from a Milli-Q water purification system (Millipore SAS, France). Calibration solutions in n-hexane solvent were prepared immediately before use. As internal standards 5-fluoroacenaphththylene, 1-fluoropyrene, 9-fluorobenzo[k]fluoranthene at a concentration of 10 μg/ml in toluene were used.

4.5. PAHs extraction

For the determination of PAHs samples were subjected to the solvent extraction. The water sample (~600 ml) was transferred to a 1-L glass separatory funnel and shaken for five minutes with 4 mL of n-hexane, followed by the collection of the n-hexane phase. The extraction step was repeated twice and the solvent extracts were combined. Anhydrous Na$_2$SO$_4$ was used to remove

residual water from the extracts. The samples were then evaporated at room temperature (20 °C) under nitrogen flow using a multi-channel evaporator (Liebisch, Bielefeld, Germany). Subsequently 1 ml of n-hexane was added and the samples were subjected to final determination by GC-MS analysis.

4.6. PAHs extraction using Solid Phase Microextraction (SPME)

The SPME apparatus is a very simple device (Fig. 6). It consists of a fibre, 1 cm in length bonded to a stainless steel plunger and installed in a holder (King et al., 2003). PDMS-coated fiber was chosen for the extraction of the target analytes investigated in this work, since it provides well-defined absorptive retention, high permeability and good thermal stability (King et al., 2004; Vas and Vékey, 2004; Ouyang and Pawliszyn, 2006; Witt et al., 2009; Kirso et al., 2011). Prior to use fibers were conditioned in the injection port of a GC for 2 h according to instructions provided by the manufacturer. More than 100 samplings were completed with the same fiber with no lost in the sensitivity. For SPME extractions 40 mL of sample on 40 mL vials capped with PTFE-coated septa were used. Fiber was inserted in a sample using a syringe needle that pierced the septum (Fig. 7). The needle was carefully removed and the position of the fibers was adjusted so that fiber remained in the sample water during extraction. Retracting the fiber into the needle through the septum terminated the extraction. The SPME device was transferred immediately to the GC-MS, where analysis was carried out (Fig. 7). Each sample was analyzed minimum in triplicate.
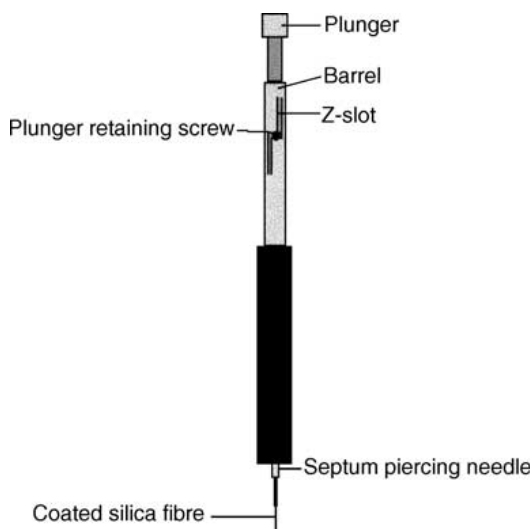

Figure 6. Components of SPME (King et al., 2003).

Extraction procedure

Pierce septum on sample container.

Expose SPME fiber/ extract analytes.

Retract fiber/ withdraw needle.

Desorption procedure

Pierce septum in GC inlet (or introduce needle into SPME/HPLC interface).

Expose fiber/ desorb analytes.
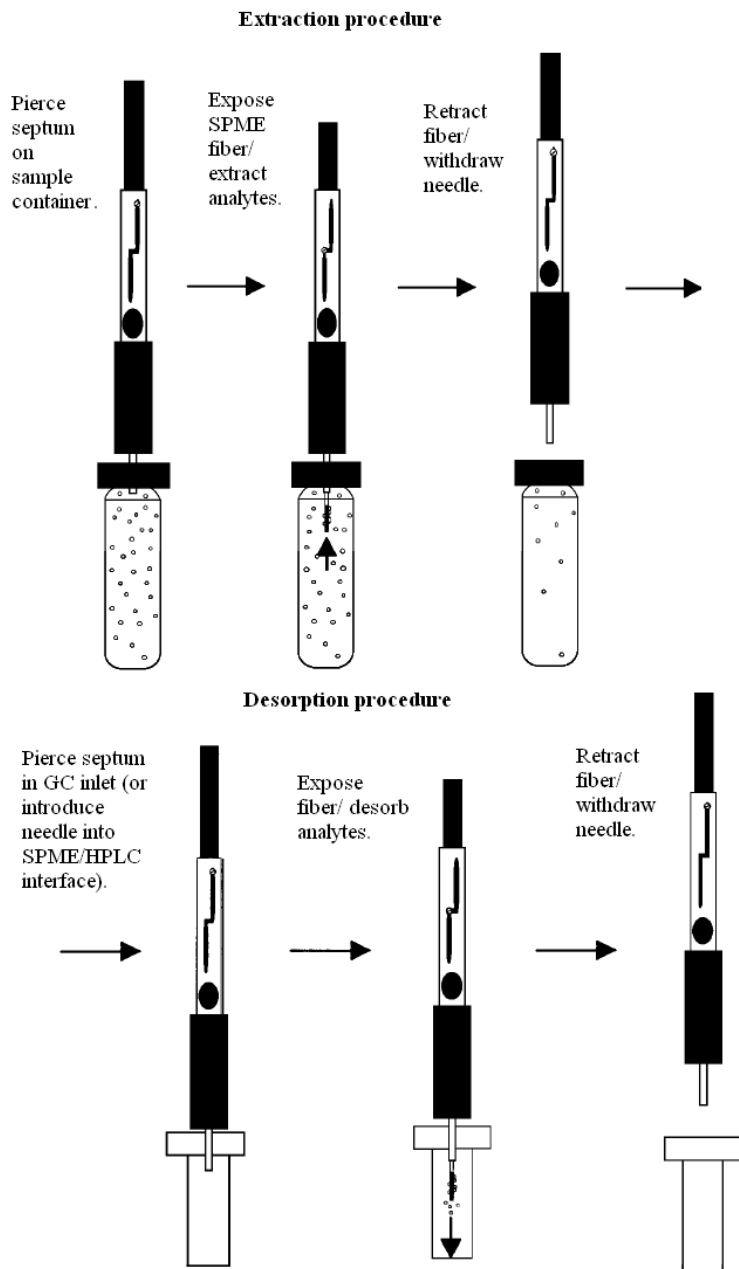
Retract fiber/ withdraw needle.

Figure 7. SPME extraction and desorption procedures (Supelco Bulletin 923).

4.6.1. Optimization of SPME parameteres

Injector temperature, injection depth, desorption time are parameters, which should be optimised when SPME is coupled to GC-MS. The highest operating temperature recommended for the fiber by the supplier is 280 °C, and conditioning temperature is 250 °C. The injector temperature of 250 °C was used for desorption due to highest desorption efficiency and prolonging the lifetime of fiber. On several occasions, some compounds would retain on the SPME fiber after injection in the GC-MS, which is known as carry-over effect. Thus, blank desorption of the fiber were carried out to ensure contamination-free situation was present both before and during use. If the fiber was exhausted the conditioning of the fiber was performed for 15–30 minutes. To find hottest part of the GC injector series of experiments were carried out with desorption phenomena at different depths of injector, keeping the other parameters constant. A depth of 2.5 cm has been chosen in all further experiments because it provided maximum desorption efficiency. Thermal desorption time was studied by leaving the fiber in the injector for progressively longer periods of time, after it had been exposed to the same concentration solution with identical absorption parameters. For complete desorption of the compounds the three minutes at 250 °C was used. No further improvement was observed when desorption time was increased. Blank desorption of the fiber were done to avoid contamination during usage.

4.6.2. SPME extraction conditions

There are a number of factors that may influence the efficiency of the SPME technique including the fiber exposure time, temperature and agitation during exposure (King et al., 2004; Tang and Isacsson, 2008; Kirso et al., 2011). In the present study three extraction temperature levels were examined: 20 °C, 45 °C and 60 °C. The sorption time profiles were studied by monitoring the peak area as a function of exposure time immersing the fiber to the sample during 10, 30 and 60 min. Optimal time is the shortest time to reach equilibrium or an amount high enough to obtain proper quantification (Eriksson et al., 2001; Tang and Isacsson 2008). Previous studies demonstrated that agitation of the sample during fiber exposure enhances extraction (King et al., 2004; Tang and Isacsson, 2008), so magnetic stirring for agitation (800 rpm) was applied in all experiments. In all cases, the SPME device was transferred immediately to the GC-MS, where analysis was carried out using the method described previously. Each analysis was carried out in triplicate.

A sample of spent shale field leachate (pH 7.15, TDS 496 ppm) from oil shale waste disposal was employed to select optimal SPME extraction conditions for determination PAHs C_{free}. Effect of temperature on the extraction efficiency is presented in Fig. 8. When the temperature was raised up to 45 and 60 °C the extracted amount of AC and ACN increased, whereas for FL, PHE,

FA and PY no further extraction efficiency improvement was observed (extraction time 30 min). This could be explained by the PAHs' desorption from the fiber at high temperatures. Extraction temperature 20 °C was chosen in this study and was used for further experiments, suggesting the best recovery for the most compounds. Furthermore, these experimental conditions could give more realistic data on PAHs bioavailability in environmental matrices. Longer sampling time increased the extraction efficiency of all compounds studied (Fig. 9). Higher ring PAHs was not found in free form. It could be explained by that heavier PAHs have tendency to bind with organic and mineral (colloid, clay) matter due to very low solubility of these compounds. The 30-min extraction time chosen for further experiments is a compromise between sensitivity and sufficiently short extraction time. Longer extraction time was not studied in order to avoid the excessive extension of the analysis time. The final conditions selected were: injector temperature 250 °C, injector depth 2.5 cm, desorption time 3 minutes, magnetic stirring (800 rpm), and extraction time – 30 minutes at 20 °C. SPME can be approached as a partition or equilibrium extraction technique. A non-equilibrium determination SPME was implemented during the experiment. As the extraction conditions chosen are below the equilibrium time, slight changes in variables, such as temperature, time and stirring rate can change the results. Neither complete extraction of analytes nor full equilibrium is necessary; however consistent SPME analysis parameters are critical for accurate results (Heringa and Hermens, 2007; Tang and Isacsson, 2008). Efforts necessary were made to hold these variables precisely for every sample in order to maintain the comparable results.
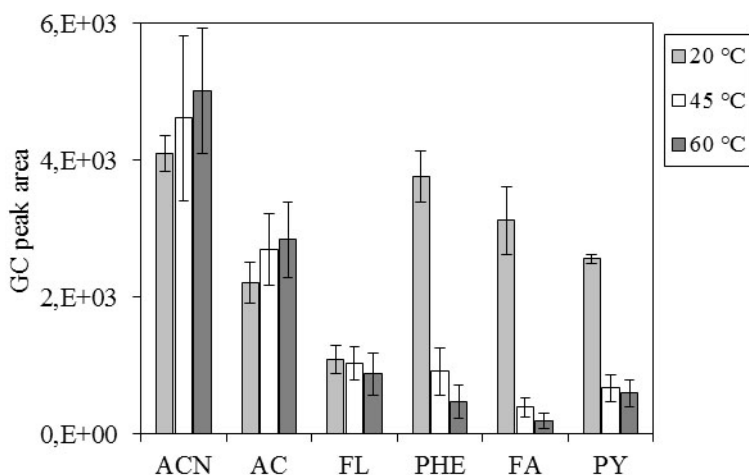

Figure 8. Effect of the temperature on amount of PAHs extracted at 30 min. The vertical lines represent standard deviations.
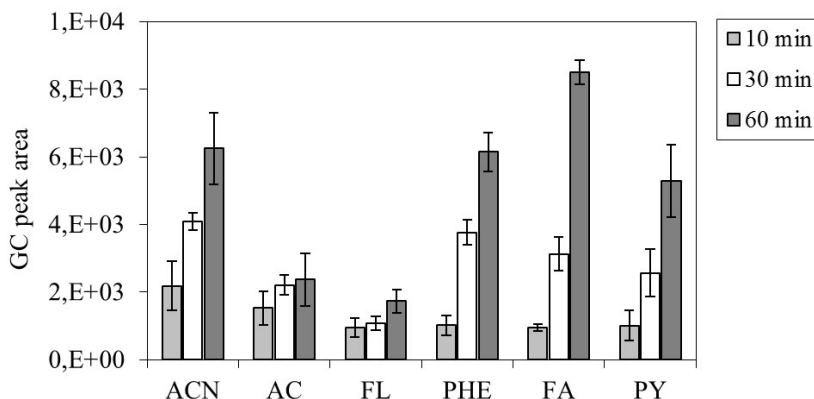
Figure 9. Effect of the extraction time on amount of PAHs extracted at 20 °C. The vertical lines represent standard deviations.

4.6.3. Validation of the SPME method

The linearity of the SPME-GC-MS method was tested in SIM mode by extracting aqueous standards with concentration between 0.001 and 1.0 µg/l under optimized SPME conditions. Calibration solutions were made using standard additions of the PAHs mixture to distilled water. The calibration curves show excellent linearity with the correlation coefficient ranging between 0.96–0.99 for all standards. The external standards were analyzed under the same conditions as the samples concerned. The relative standard deviation (RSD) averaged 14% (range 2–25%) for real leachate samples, which includes variation between SPME sampling, manual injections and instrumental analysis. The limit of detection (LOD) and limit of quantification (LOQ) were from 0.1 to 1 ng/l and 1 to 10 ng/l, respectively. As a rule, the higher RSD, LOD and LOQ values were determined for compounds having higher molecular mass. To confirm the applicability of the SPME method to extract PAHs from real water samples, SPME-GC-MS method recovery was obtained from the ratio of spiked real water sample to spiked ultrapure water. Both samples were extracted by SPME according to the optimized method. The relative recovery obtained was observed to be good: 91–104%. Blank tests were done on ultrapure water, which was extracted by SPME according to the optimized method to assess contamination from reagents and materials.

4.7. PAHs determination by GC-MS

An Agilent HP 7890 GC (Palo Alto, CA, USA) with a HP-5MS capillary column (30m × 0.25mm × 0.25µm) and a Model 5975B mass-selective detector was used. Agilent G1701DA GC/MSD Chemstation software was applied for the treatment of data. The GC oven temperature program was as follows: 60 °C

for 0.8 min, then 15 °C/min to 320 (total run time 20.13 min). The MS was operated both in full scan and selected ion monitoring (SIM) mode. The target compounds were analysed in SIM mode, using the molecular ion and one qualifier ion for each compound. Full-scan acquisition was used for compound confirmation. The GC was operated in the splitless mode (splitless time – four min). Helium (99.99%) was used as a carrier gas. Blank tests were done on ultrapure water, which was extracted according to the current method to assess contamination from reagents and materials. The limit of detection (LOD) and limit of quantification (LOQ) were in the range 0.001–0.01 µg/l and 0.01–0.1 µg/l, respectively. The relative standard deviation (RSD) averaged 9.1% (range 0.4 – 34.7%) for leachate samples. Average RSD of individual compounds were (in %): NA 4.0, ACN 10.5, AC 5.7, FL 11.4, PHE 6.9, AN 12.2, FA 12.3, PY 8.3, B[a]A 11.4, CHR 13.1, B[b]F+B[k]F 8.2, B[a]P 18.0, B[g,h,i]P 15.5 (for abbreviations see Table 1).

4.8. Monofluorinated PAHs (F-PAHs) as internal standard

It is generally accepted that the accurate determination of micro contaminants in such complex mixtures as wastes requires the use of external, or preferably, internal standards. For PAHs labeled isomers are generally recommended as internal standards. However, some problems arise due to the possibility of scrambling of deuterium and hydrogen atoms. Recently monofluorinated PAHs (F-PAHs®) were synthesized. They are considered to be a promising alternative to isotope labeled internal standards because they are closely similar to the parent PAHs in terms of chemical and physical properties do not occur in the natural environment and are not being produced in appreciable amounts for any industrial, medical or other related purpose (Luthe et al., 2003). Representatives of F-PAHs, i.e. fluoronaphthalene and 2-fluorobiphenyl, are already recommended as internal standards in the EPA 8100 method for determination of PAHs.

The application of F-PAHs (obtained from Chiron, Trondheim, Norway) as internal standards in GC-MS analysis for PAHs in oil shale wastes, particularly on combustion ash, was performed at the first time for that sort of matrix. Three F-PAH compounds were used as internal standards, i.e. 9-fluorobenzo[k]fluoranthene, 1-fluoropyrene and 5-fluoroacenaphthylene (F-B[k]F, F-PY and F-ACN). Certified reference materials play an important role in verifying the accuracy and establishing calibration of analytical methods. Therefore, at the start, the suitability of F-PAHs as internal standard was tested on the set of certified 16 priority PAHs, then the water extracts of ash samples were analyzed. Retention time and qualifier ions were determined before the calibration procedure.

Calibration solutions were prepared with the 16 EPA PAHs mix. F-PAHs were used as internal standards. The linear range was established by five-point (as a minimum) calibration curves in the range of 0.1–1.0 mg/ml, each calib-

ration level was spiked with internal standards. Use of the internal standards increased the precision of calibration (R^2 values of calibration curves with only external standards were in the range 0.95–0.96, and more than 0.98 when F-PAHs were used). Using the method described above the following pairs of compounds, e.g., B[b]F and B[k]F; D[a,h]A and IP; AN and PHE, were not successfully resolved and separated. However, the purposes of the analysis can be served by reporting the sum of an unresolved PAHs pair. This problem is not new, is described before and can be solved, for instance, by using liquid-crystalline polysiloxane columns (Poster et al., 2006).

The chromatograms of the certified PAHs mix demonstrated that two compounds, F-PAHs, i.e. F-B[k]F and F-ACN, fitted well as internal standard for the certified analyte tested. The chromatographic data for the F-PY varied among identical measurements, therefore, F-PY could not be used as internal standard for determination of PAHs in the described conditions. Additionally, Nagy et al. (2008) mentioned another problem of using F-PAHs as surrogate standards in the analysis for PAHs in surface water and sediment samples when the internal standard was added to the system before the separation phase. They found that F-PY could not be extracted from sediment samples, but can be successfully used for water samples. For the additional testing of the method, the water extracts of oil shale ash were analysed for PAHs. In these samples the presence of miscellaneous traces as other combustion related compounds greatly affected the intensity of F-ACN peaks and was not equal for all samples. Therefore, in our case only one internal standard F-B[k]F could be used for quantification of PAHs contents in oil shale solid wastes. Nevertheless, the results obtained by using only one F-PAH as internal standard are quite satisfactory. Consequently, the analytical method described in the present study is a rapid and simple procedure that allows reliable determination of PAHs. This method, based on the technique using F-PAHs as internal standards and GC-MS as the analytical technique, was validated by means of certified reference samples.

4.9. Metals determination

Samples of fresh and aged spent shale (á 0.25 g) were digested in 3.5 mL (4.9 g) concentrated HNO_3 Scan Pure grade) using a Multiwave 3000 microwave oven (Anton Paar, Austria) with a program running at 1000 W for 1 minute followed by 350 W for 10 minutes. The digested samples were diluted with distilled water to 0.1 M HNO_3 in a separate vessel to a final volume of 460.8 mL. The samples were then decanted to 14 mL polypropylene tubes for further analysis by ICP-MS (Thermo Element 2, Germany). The following parameters of leachates were determined: pH, conductivity (EC) and concentrations of Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Rb, Sb, Sr, Tl, V and Zn. The leachates were preserved with 0.1 M HNO_3 and analysed directly by ICP-MS (Thermo Element 2, Germany). Blank tests without sample but applying the same procedure were carried out in parallel for each set of analyses.

5. RESULTS AND DISCUSSION

5.1. Field leaching

5.1.1. General characterization of leachates from fresh and aged spent shale deposit

The leachate samples were clear and colourless when assessed visually. The leachates were alkaline, with pH varying from 7.34 to 10.58 (Table 7). pH of leachates was higher in the case of aged spent shale, both the average value and the maximum value. Different pH in leachates from the active and closed disposal can be explained by differences in fresh and aged waste composition due to the technological processes involved in oil production and aging of land-filled material (Sedman et al., 2012; Irha et al., 2013). The average content of inorganic soluble components in leachates, estimated from the measured EC, was lower in leachates collected from aged waste material compared to leachates of fresh waste material (Table 7). The most obvious reason of EC decrease with time is more compacted solid matter of aged spent shale due to changes of composition and properties (Mõtlep et al., 2007; Sedman et al., 2012; Paper III).

Table 7. pH and conductivity (EC) values observed in field leachates collected at spent shale deposit over the period 2006 – 2009.

Parameter	Aged spent shale		Fresh spent shale	
	Average ± SD	Range	Average ± SD	Range
pH	8.22 ± 0.89 (25)[*]	7.47 – 10.58	7.82 ± 0.22 (10)	7.34 – 8.10
EC, mS	1.81 ± 0.51 (25)	0.50 – 4.53	4.33 ± 1.93 (10)	2.43 – 7.94

[*] number of samples

5.1.2. Distribution of PAHs in leachates

Table 8 shows the average PAHs concentrations detected and quantified in the field leachates, including range of concentrations. Among EPA's 16 priority PAHs in the leachates the following compounds were identified in the leachates: NA, AC, ACN, FL, PHE, AN, FA, PY, B[a]A, B[b]F, B[k]F, B[a]P, B[g,h,i]P (Table 8, for abbreviations see Table 1). The sum of determined PAHs is also presented in Table 8. NA showed the highest detection frequency, followed by PHE and ACN. Among all determined PAHs, ACN followed by PHE, PY and B[a]A showed the maximum concentration. Detection frequency and content of low molecular weight PAHs were as a rule higher than those of high molecular weight compounds (Table 1). The reason of higher mobility of low molecular weight PAHs is their higher water solubility (Table 1). PAHs with lower hydro-phobicity such as NA are more likely to be released to the leachate water. Water solubility of PAHs with two to six rings decreases over five orders of magnitude

with increasing molecular weight (Table 1) and they are found almost exclusively associated with solid phases. Low water solubility results in a high affinity of PAHs to solid matter. Other studies have also observed that the fraction of PAHs associated with colloids and/or organic matter increases dramatically with molecular weight, leading to long residence time in a landfill (Kraaij et al. 2003; Hawthorne et al. 2005; Kalmykova et al., 2013).

Table 8. Concentration of PAHs (µg/l), number of samples (n), and samples with concentration above the detection limits (>d.l.).

PAHs	Aged spent shale		Fresh spent shale	
	Range (average)	n (>d.l.)	Range (average)	n (>d.l.)
NA	3.1 – 107.8 (20.5)	25 (25)	6.1 – 37.8 (14.8)	7 (7)
ACN	3.3 – 164.5 (25.2)	25 (19)	11.2 – 26.3 (19.8)	7 (4)
AC	2.8 – 19.4 (8.1)	25 (16)	2.4 – 9.2 (6.4)	7 (5)
FL	1.2 – 21.0 (10.6)	25 (14)	0.9 – 15.9 (10.0)	7 (3)
PHE	3.2 – 124.2 (34.7)	25 (24)	4.3 – 49.5 (19.0)	7 (7)
AN	6.2 – 46.5 (21.4)	25 (10)	7.9 – 9.8 (8.6)	7 (3)
FA	6.3 – 19.9 (9.2)	25 (6)	6.2 – 13.9 (8.8)	7 (4)
PY	4.8 – 116.6 (7.7)	25 (13)	5.8 – 15.7 (13.4)	7 (5)
B[a]A	1.2 – 115.3 (26.8)	25 (6)	4.1 – 4.2 (4.2)	7 (2)
B[b]F+B[k]F	0.5 – 80.0 (10.2)	25 (12)	0.5 – 3.4 (2.3)	7 (4)
B[a]P	0.4 – 1.5 (0.9)	25 (9)	0.7 – 3.0 (2.0)	7 (3)
B[g,h,i]P	1.5 – 1.9 (1.6)	25 (4)	1.2 – 2.9 (2.1)	7 (7)
Sum of PAHs	19 – 315 (109)	–	36 – 151 (65)	–

The release of PAHs from the deposited spent shale in our study was estimated and comprised 2–41 µg/kg for aged spent shale, and 3–11 µg/kg for fresh spent shale. Previously reported values of PAHs in fresh spent shale samples are between 8.2–13.3 mg/kg, and in aged spent shale samples 9.4–13.3 mg/kg (Otsa and Tang, 2003; Saether et al., 2004), indicating their general persistence in the environment. The distribution of PAHs in solid matter is presented in Table 2.

Some of the studied PAHs (B[a]P, B[k]F, B[b]F, B[g,h,i]P) have been iden-tified as priority hazardous substances by EU legislation (Decision No 2455/2001/EC) and some (B[a]P, B[a]A, B[k]F, B[b]F) have been classified by US EPA as probable human carcinogens (NTP, 2005). Levels of PAHs in the leachates generally exceeded the European Environmental Quality Standards (Directive 2008/105/EC) for NA, AN, FA, B[b]F, B[k]F, B[a]P, B[g,h,i]P. Despite the low concentrations of PAHs in leachates they can reach un-acceptable levels over longer periods of time due to accumulation. The recom-mendation of EPA and other authorities for priority PAHs is to decrease their concentration in environment. In the studied landfill the leachate water is collected and conveyed to the sewage treatment plant. Currently, the situation on the waste heaps is changing and now part of spent shale deposits is closed (http://www.envir.ee/1172371).

Sampling points from aged part of deposit (3A) and from active part of deposit (1F) were chosen to represent changes during field experiment. Total concentrations and distribution profiles of 16 EPA's priority PAHs in leachates are presented in Figs. 10–11. Sum of determined PAHs ranged from 25 to 263 µg/l in leachates from sampling point 3A, and from 41 to 130 µg/l in leachates from sampling point 1F. The sum of PAHs from the sampling point in aged spent shale (3A) was generally higher than from the corresponding sampling point in fresh spent shale (1F) at the same sampling time (Fig. 11). However, while the leaching of PAHs from the aged spent shale clearly decreased during the entire sampling period, the corresponding leaching from the fresh spent shale approached a constant level over the last year of sampling. The distribution of monthly average precipitation and temperature over the sampling period shown in Fig. 4 might help explain the changes in PAHs mobility. The highest sum of PAHs in leachate water was recorded in samples collected during the year of 2007, when higher average temperature and lower rainfall was recorded (Fig. 4). During the period of higher precipitation (2008–2009), concentrations of PAHs were lower in all samples (Table 8, Fig. 4). Apparently the leachate became more diluted during rain events.

The distribution of PAHs was different in the two sampling points (Figs. 10, 11). For instance leaching of AN was observed mainly from the sampling point 3A in the closed part of deposit, whereas ACN leached mostly from sampling point 1F in the active part of the deposit. Interesting to point out, that remarkable are correlations between PAHs leached from sampling point 3A and their concentration in solid waste (Table 1) in Nov06/Sep07, Sep07/June08, June/Sep08, Apr/Oct09 for low molecular weight detected PAHs ($R^2 > 0.9$) except NA. Thus PAHs leaching at field conditions depends on the characteristics of the deposited waste and sampling point, sampling time, as well as weather conditions.

The sum of priority PAHs in leachates varied significantly throughout the study period, ranging from 19 to 315 µg/l for aged and 36 to 151 µg/l for fresh deposits, respectively. According to the average concentrations of individual PAHs in the field leachates (Table 8) the aged spent shale deposit leached higher amounts of PAHs (NA, AC, ACN, FL, PHE, AN, FA, B[a]A, B[b]F, B[k]F) than fresh spent shale. Relative abundances of individual PAHs in leachate samples from aged and fresh spent shale differed from each other. PHE showed the highest mean (34.7 µg/l) in fresh spent shale (Table 8), whereas in the aged spent shale ACN was highest (19.8 µg/l). B[a]A and AN leached more from aged waste and AC and FL from the fresh one. In the higher molecular weight group B[a]P and B[g,h,i]P leached from fresh waste. In the present study however the concentration of PAHs in leachate water from aged deposit is higher than from the fresh one, indicating that aging of the deposited waste does not lead to immobilization of PAHs presented in spent shale. The results show negative correlation between log K_{oc} and PAHs concentration in leachate from the fresh spent shale. Interestingly, the correlation between EC values and PAHs concentration in leachate water from fresh spent shale was found ($r^2 \approx 0.7$).
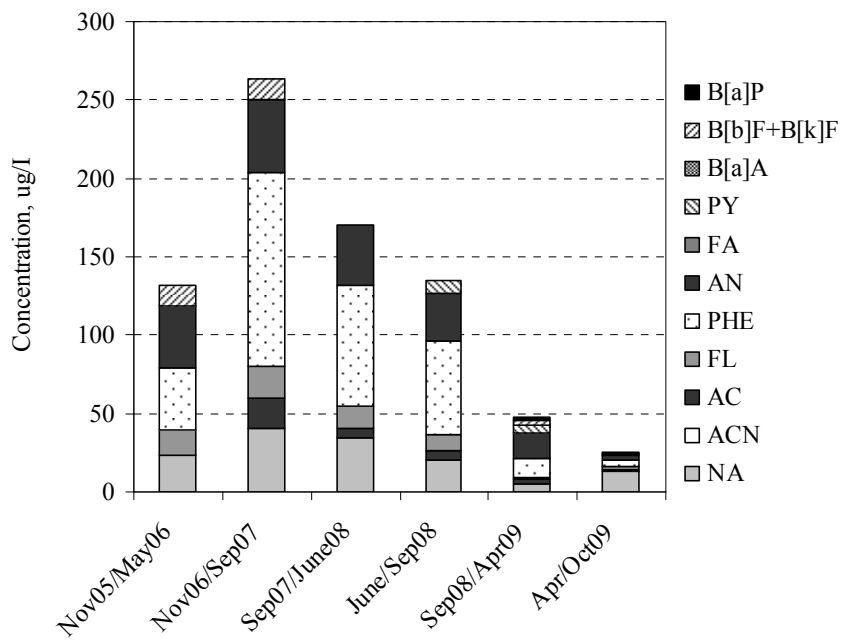
Figure 10. Total content and concentration profile of detected PAHs in field leachates from sampling point 3A (closed part of deposit).
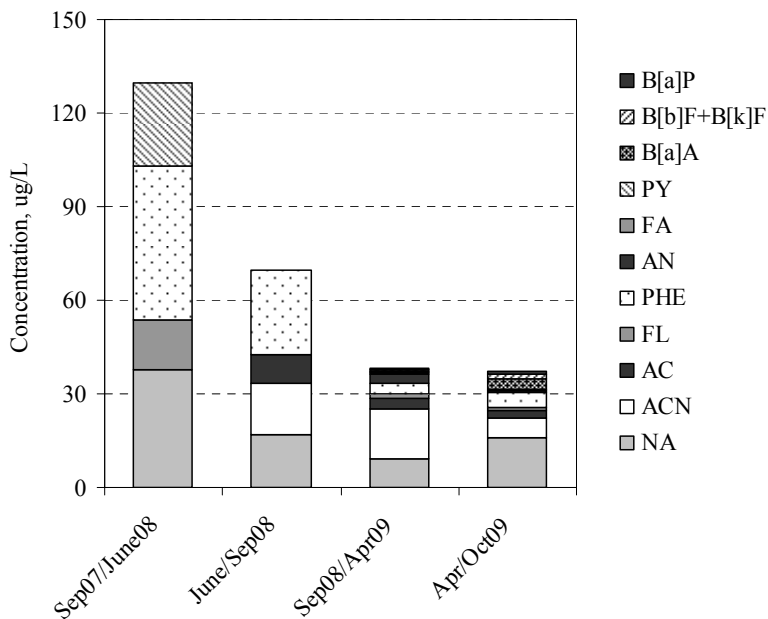

Figure 11. Total content and concentration profile of detected PAHs in field leachates from sampling point 1F (active part of deposit).

Increased leaching of PAHs from the aged spent shale depended on the properties of PAHs and characteristics of the waste matter. Sorption to the soot, charcoal and other fractions has been observed to be up to 10–1000 times stronger than sorption to 'other' organic matter influencing PAHs leachability (Mukherji et al., 1997; Accardi-Dey and Gschwend, 2002; Jonker and Barendregt, 2006; Paper I). It is therefore suspected, that bitumen might also play an important role in the actual environmental sorption processes in spent shale deposit. According to Otsa and Tang (2003) during the aging of spent shale the bitumen content decreases (Table 9). Bitumen can act as a sorbent for PAHs in spent shale deposit, and consequently the decrease of bitumen content can explain the increased leaching of PAHs from aged waste material. Thus, the leaching of PAHs from both spent shale deposits depended on solid matrix properties and conditions in a given sampling site.

Table 9. Content of bitumen in three samples of fresh spent shale and four samples of spent shale from landfill (Kohtla-Järve) (Otsa and Tang, 2003).

Nr	Location of sampling point	Sampling time after landfilling	Bitumen content, %
1	Fresh	–	3.95
2	Fresh	–	2.02
3	Fresh	–	2.70
4	Landfill	One year	1.36
5	Landfill	Three years	1.44
6	Landfill	Five years	2.63
7	Landfill	Ten years	0.99

5.1.3. Bioavailable PAHs' determination by SPME technique

Samples of leachate from the disposal were subjected for analysis of PAHs C_{total} by conventional solvent extraction and C_{free} by developed SPME method (Table 10). Both C_{total} and C_{free} of PAHs in field leachate were found to vary with two and three ring PAHs predominating. PAHs C_{total} ranged from 1.26 to 77.56 µg/l (Table 10). In bioavailable form the following PAHs were found: ACN, AC, FL, PHE, AN, FA and PY. PAHs C_{free} was found to vary between 2.38 and 62.35 ng/l. It is important to note, that not only low ring PAHs compounds presented in Table 10 leached from the disposal, but also five and six ring PAHs (B[a]A, B[k]F, B[b]F, B[a]P, B[g,h,i]P) were found in leachates in trace concentration in some samples. Five and six ring PAHs were not detected in free dissolved form in current experimental conditions. The absence of heavy PAHs in bioavailable form in the leachate samples is indicative of their strong binding to the dissolved or solid matter (Otsa and Tang, 2003; Enell et al., 2004; Van der Wal et al., 2004; Ter Laak et al., 2006). Meanwhile, other investigators have also observed, that the fraction of PAHs associated with colloids and/or organic matter increases dramatically with number of rings (Kraaij et al., 2003; King et al., 2004; Hawthorne et al., 2005).

Table 10. Total dissolved concentrations (C_{total}, µg/l); freely dissolved concentrations, (C_{free}, ng/l) of PAH in field leachates of spent shale; C_{free}/C_{total} – fraction of bioavailable PAH in percents (Paper II).

	ACN	AC	FL	PHE	AN	FA	PY
Sample A							
C_{total}	11.12(2.3)[a]	4.02(2.0)	1.26(9.2)	12.17(16)	bc	8.24(3.5)	9.44(7.6)
C_{free}	5.68(15.6)	39.10(5.4)	34.08(6.1)	58.78(3.1)	23.49(0.4)	2.38(0.2)	5.38(24.2)
C_{free}/C_{total}	0.05	0.97	2.70	0.48	–	0.03	0.06
Sample B							
C_{total}	6.35(4.1)	2.81(5.7)	1.35(13.7)	8.21(0.3)[b]	44.35(19.0)	7.87(4.5)	9.34(6.0)
C_{free}	6.46(23.0)	22.73(3.9)	18.29(0.4)	43.8(21.8)[b]		nd	1.2(18.8)
C_{free}/C_{total}	0.10	0.81	1.36	0.53[b]	–	–	0.01
Sample C							
C_{total}	12.16(0.8)	6.30(5.5)	14.05(20.5)	77.56(7.1)	38.04(25.0)	nd	nd
C_{free}	13.05(4.9)	43.16(6.2)	30.44(9.0)	62.35(8.3)	38.78(7.7)	nd	nd
C_{free}/C_{total}	0.09	0.01	0.04	0.12	0.10		

[a] (RSD in percents), [b] PHE+AN, bc – below calibration level, nd – not detected

The distribution ratio, defined as relation C_{free}/C_{total} quantifies the difference between relevant for transport C_{total} and for uptake by biota C_{free}. According to obtained results (Table 10) only 0.01–2.7% of C_{total} of studied PAHs in the samples comprised for C_{free}. C_{free} is a small fraction of C_{total}, indicating strong association of PAHs with organic and mineral (colloid, clay) matter. A study by Cornelissen et al. (2009) determined C_{free} and C_{total} of PAHs in leachates from municipal sanitary landfill. These researchers found that 0.1–20% of PAHs were freely dissolved, demonstrating that our findings are in close agreement. The heterogeneity of the target material caused not only differences in PAHs release, but also the differences in general characteristics of spent shale leachates. pH of field leachate in the samples A, B, C were 7.7, 8.4, 12.2, respectively. Electrical conductivity of water is directly related to the concentration of TDS in the water, and the values for the samples A, B, C were 0.25, 0.26, 1.6 ppt, respectively. Differences in distribution of PAHs of C_{total} and C_{free}, pH and TDS in leachates from the disposal concerned can be explained by non-homogenous nature of the parent material, caused by different rate of weathering.

5.1.4. Metals in field leachates

Concentrations of potentially harmful trace elements in field leachates from aged and fresh deposition fields are presented in Table 11. Leachates from closed part of deposit contained comparable concentrations of Cu, lower concentrations of Co, Cr, Mo, Ni, Pb, Zn, and slightly higher concentrations of V compare to leachates from active part of deposit. The most mobile among the studied elements were Mo, Zn, Ni, Cu, Cr and V. Their average concentrations in leachates from closed part decreased as following: Mo > Ni ~ Zn > Cu ~ Cr > V. In case of leachates from the active part of the deposit the order of elements was the following: Mo > Ni > Zn > Cr > Cu > V. The highest concentration of Mo (104 µg/l), Zn (80 µg/l) and Ni (76 µg/l) were found in leachates from active part of deposit. Remarkably, the molybdenum exhibited highest mobility although the absolute amount of Mo in spent shale is relative small (Table 4). Among other heavy metals relatively high concentration of Ni was detected, while almost negligible concentrations for Pb and Cd were observed. Comparison the average concentrations of the most mobile elements in leachates (Table 11) suggest that during the time the burden on the surrounding environment by Ni, Mo, Cr and Zn decreased and at the same time the burden by Cu and V slightly increased.

For the majority of the analyzed compounds, the studied leachate samples were within the concentration ranges previously published for landfill leachates (Baun and Christensen, 2004; Baumann et al., 2006; Matura et al., 2010). The leaching of elements in both spent shale deposit area depended on solid matrix properties and conditions in specific sampling site.

In leachates from closed part of deposit significant correlation was observed between Mo and Ca, K, Sr, Rb, Ba, Cr and V. Positive correlation between Ni

and precipitation (p<0.05) was found. Zn correlated with Fe, Ba, Cr, Cu and Pb. Cu correlated with Cd and Cr. Correlation between V and elements Mn, Cr, Mo and Ni was observed. In the case of leachates from closed part of deposit good correlation was found between Mo and Ca, Mg, Mn and positive correlation between Mo and Fe (Table 11). Also correlation between V, Zn and Mg, Ni and Cr was found.

The obtained data suggest noticeable role of soluble Ca, Fe/Mn containing components i.e. inorganic colloids on transport of trace elements in spent shale deposit. Metals are well known to bind to colloidal matter present in leachate and groundwater (Bertsch and Seaman, 1999; Citeaue et al., 2003; Baun and Christensen, 2004; Kretzschmar and Schäfer, 2005; Baumann et al., 2006; Baumann, 2007; Pédrot et al., 2008; Matura et al., 2010). When associated with colloids, metals show significantly different transport properties compared to dissolved metals. In soils and aquifers, mobile colloidal particles originate mostly from in situ generation of submicron-sized mineral and organic matter particles, which are naturally present (Citeaue et al., 2003; Kretzschmar and Schäfer, 2005; Matura et al., 2010). Such particles can be composed of clay minerals, mineral precipitates (e.g. Fe, Al, Mn, or Si oxides and hydroxides, carbonates, phosphates), organic biopolymers (e.g. humic and fulvic acids, polysaccharides etc.) and biocolloids (Baumann, 2007). Colloids in the disposal sites reflected the waste composition and degradation (Baun and Christensen, 2004; Baumann, 2007; Matura et al., 2010). Taking into account the data of the literature and characteristics of spent shale we assume also a significant role of inorganic colloids in transport of metals in waste disposal. According to (Bertsch and Seaman, 1999) mobile colloids can be generated by a number of mechanisms, including precipitation of colloidal size phases, dissolution of cementation agents composed of fine-grained crystalline and poorly crystalline secondary minerals, and release from materials via physicochemically controlled dispersion processes.

Nevertheless, despite the concentrations of elements in field leachates are below the regulation standards, the spent shale deposit can be stable source of potentially hazardous elements (Stark and Redente, 1990; Rooney et al., 2007), particularly Mo, Ni and Zn. In the study (Stark and Redente, 1990) was observed increase of Mo concentration in plants growing on retorted oil shale disposal sites. Rooney and coauthors (2007) demonstrated that with increasing pH of soil solution soluble Ni became more toxic to plants (Paper III).

Table 11. The concentration of selected elements (in µg/l) in leachates from the fresh and aged spent shale deposit (Paper III)

Parameter	Range (median)	
	Fresh spent shale (n[*] = 8)	Aged spent shale (n = 9)
Ca	556 350 – 967 100 (786 100)	19 800 – 626 500 (346 400)
Mg	12 300 – 172 600 (108 300)	70 – 74 700 (38 000)
K	133 700 – 894 000 (500 000)	55 900 – 153 500 (110 700)
Sr	1 310 – 4 380 (2 900)	650 – 1 610 (1 180)
Rb	230 – 1 580 (870)	110 – 430 (220)
Mo	58 – 104 (95)	15 – 76 (42)
Ba	36 – 137 (80)	26 – 109 (52)
Ni	5.8 – 76 (62)	1.49 – 68 (22)
Sb	0.3 – 1.0 (0.6)	0.3 – 0.9 (0.6)
Tl	0.1 – 0.3 (0.2)	0.01 – 0.05 (0.03)
Cd	0.2 – 0.4 (0.2)	nd[**] – 0.4 (0.1)
Co	0.1 – 5.1 (2.2)	0.08 – 1.01 (0.3)
Cr	1.1 – 7.6 (5.5)	1.03 – 6.22 (3.8)
Cu	1.2 – 9.7 (4.3)	2.4 – 8.87 (4.9)
Fe	4 – 54 (32)	1.73 – 30.4 (13.4)
Mn	0.8 – 5.0 (1.7)	nd – 1.6 (0.8)
Pb	0.01 – 3.9 (1.5)	0.1 – 1.6 (0.4)
V	1.0 – 3.8 (2.4)	0.2 – 5.8 (3.1)
Zn	1.1 – 80 (41)	3.66 – 92 (35)

[*] n – number of samples

[**] nd – not detected

5.2. Laboratory leaching

5.2.1. General characterization of leachates from oil shale ash and ash-based materials

The leaching behaviour of oil shale ash and oil shale ash-based mortars was studied according to the European standard EN 12457-2(2002) (Fig. 1). For reliable data about the environmental impact of waste-based construction materials it is important to assess the leaching behaviour during hardening time or during formation of secondary components (Kuusik et al., 2012; Mõtlep et al., 2010; Pihu et al., 2012). The leaching characteristics of oil shale ash, PF and CFB oil shale ash-based mortars with hardening periods of 7, 28 and 91 days are presented in Figs. 12–13. The leachates were highly alkaline (Fig. 12) but their pH values as well as ECs decreased with increasing hardening time and were lower than the corresponding data for the initial oil shale ash (Figs. 12, 13). The high conductivity values and high concentration of mineral components in the water indicates significant water soluble inorganic ingredients in oil shale ash samples, which were higher in the case of PF ash samples (Fig. 12). At the same time, the leaching properties of each mortar depended on the specific characteristics of ash. Similarly to the results of oil shale ash leaching

tests, the leachates of mortars were also shown to contain mainly Ca^{2+}, K^+, Na^+ and SO_4^{2-}, which contributed to their highly alkaline pH values (for more information see Paper VII). The leachable content of major ions varied depending on the type of oil shale ash and hardening period. In general, the leachable content of ions in PF oil shale ash-based mortars was more than twice that in CFB oil shale ash-based mortars (Paper VII).
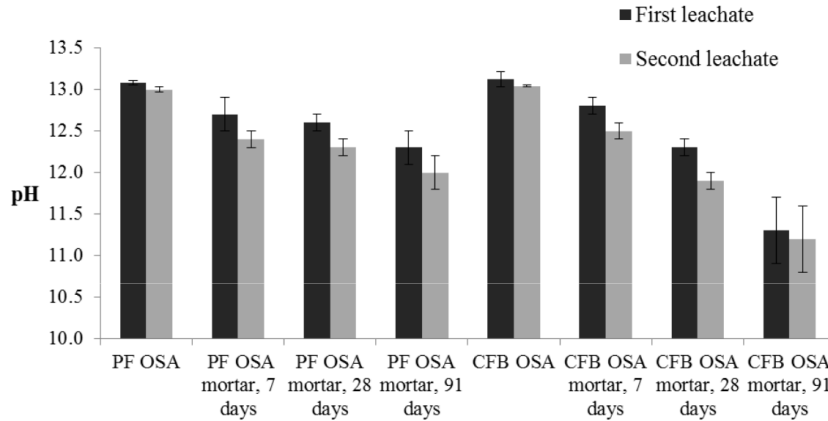

Figure 12. Average pH values of the first and second leachates from initial pulverized-fired (PF) oil shale ash (OSA) (n = 3) and circulating fluidised bed (CFB) oil shale ash samples (n = 2), and their respective oil shale ash-based mortars after 7, 28 and 91 days of hardening. Results represent the mean ± SD (Paper VII).
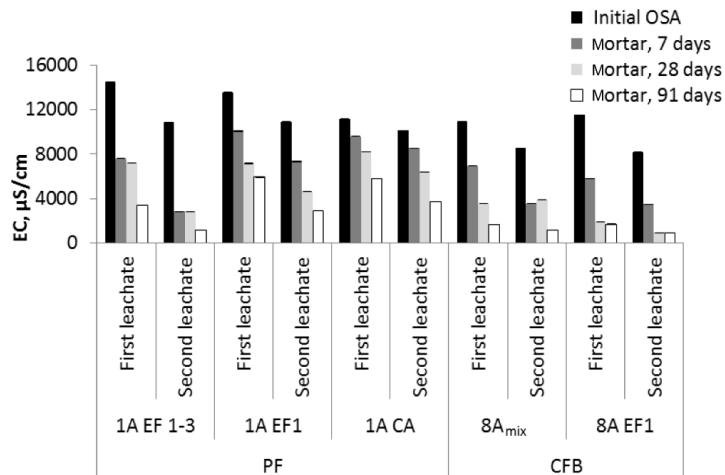

Figure 13. Mean conductivity (EC) of the leachates from initial oil shale ash (OSA) samples and OSA-based mortars after 7, 28 and 91 days of hardening. Results represent the mean ± SD of two parallel experiments (Paper VII).

The leaching behaviour of oil shale ash based concrete was studied according to the European standard CEN/TC 15862(2012) (Fig. 1). The leaching characteristics of PF and CFB oil shale ash-based concretes with hardening periods of 7, 28 and 91 days are presented in Table 12. The leachates were highly alkaline, pH values were 11.5–12.1; 10.2–11.2 and 9.3–11.3, with hardening periods of 7, 28 and 91 days, respectively. pH of CFB oil shale ash-based concretes was lower than PF ones. pH values as well as ECs decreased with increasing hardening time. The leachable content of major ions varied depended on the type of oil shale ash and hardening period. In general, the leachable content of ions in oil shale ash-based concretes decreased with increasing hardening time. pH and EC values of PF oil shale ash-based concretes leachates were higher than CFB oil shale ash–based concrete leachates.

Table 12. Average pH, conductivity (EC, µS/cm) and concentration of sum of 16 EPA PAHs (µg/l) in leachates from OSA-based concrete with respect to hardening time (the value of SD in parentheses).

Concrete sample	pH	EC	Sum of PAHs
PF/1A EF1 concrete			
7 days	11.5 (0.30)	628 (324)	0.0004 (0.0001)
28 days	11.5 (0.05)	824 (90)	0.0074 (0.002)
91 days	10.4 (0.10)	359 (87)	0.0058 (0.001)
PF/1A CA concrete			
7 days	12.1 (0.10)	3450 (570)	0.0007 (0.0002)
28 days	11.8 (0.10)	2002 (588)	0.010 (0.002)
91 days	11.3 (0.0)	1592 (64)	0.0066 (0.001)
CFB/8A EF1 concrete			
7 days	11.7 (0.05)	1212 (56)	0.0047 (0.0009)
28 days	10.2 (0.05)	734 (28)	0.0042 (0.0008)
91 days	9.3 (0.0)	490 (109)	0.0073 (0.002)

5.2.2. Distribution of PAHs in leachates

The release concentration of total PAHs in leachates from the PF and CFB oil shale ash samples are given in Table 13. The results of the experiment indicate that the concentration of more hydrophobic heavy molecular weight PAHs including mutagenic and highly carcinogenic B[a]P were lower than the detection limit (LOQ = 0.3 µg/l) of the analytical methods applied. The particle size distribution, grain shape and surface characteristics and the content of amorphous phase are the main factors, which could affect the availability of PAHs on leaching. Concentration of the sum of PAHs in leachates was higher for PF ash samples if compare with CFB ash samples. The mobility of PAHs from CFB and PF oil shale ash is 20.2% and 9.9%, respectively. The concentration of PAHs in all leachates was below the threshold limit values of groundwater quality (0.2 µg/l for the sum of PAHs) (RT I, 2010).

Table 13. Average pH, EC (µS/cm) and concentration of individual PAHs (µg/l) in leachates from oil shale ash samples, the value of the SD in parentheses (for abbreviations of oil shale ash type see Table 6).

PAHs	PF/1A EF1	PF/1A EF1-3	PF/1A CA	CFB/8A EF1	CFB/8Amix
NA	0.014	0.020	0.002	0.002	0.004
	(0.003)	(0.004)	(0.004)	(0.006)	(0.008)
AC	0.004	0.005	0.001	nd[*]	nd
	(0.008)	(0.001)	(0.002)		
FL	0.002	0.001	nd	0.001	0.001
	(0.0004)	(0.0002)		(0.0002)	(0.0002)
PHN	0.010	0.014	0.002	0.011	0.009
	(0.002)	(0.003)	(0.004)	(0.002)	(0.002)
AN	nd	nd	0.004	0.014	0.028
			(0.008)	(0.003)	(0.005)
FA	0.004	0.004	0.003	0.007	0.004
	(0.001)	(0.001)	(0.001)	(0.001)	(0.008)
PY	0.014	0.011	0.013	0.016	0.013
	(0.003)	(0.002)	(0.002)	(0.003)	(0.002)
Sum of PAHs	0.048	0.055	0.025	0.051	0.059

*not detected

The chemical composition of elements, time, and pH all play an important role in controlling the mobility of elements in the solid material. The leaching of sum of detected PAHs from PF and CFB oil shale ash-based mortars with hardening time 7-, 28- and 91-days are presented in Table 14. Low molecular weight PAHs (NA, AC, PHN, FL, AN) and PY leached from all mortar and concrete samples, irrespective of hardening period. AN, FA, NA are included as priority substances in the List of priority substances in the field of water policy (Directive 2013/39/EU, 2013). AN is identified as a priority hazardous substance.

The PAHs' concentration in leachates from hardening 7-, 28- and 91-days concrete samples are presented in Fig. 14. The leaching of PAHs from concrete samples was small (sum of detected PAHs was less than 1 $\mu g/m^2$). However, it was possible to detect specific PAHs in leachates: NA, FL, PHE, AN, FA, PY, CHR (for abbr see Table 1). The leached concentrations from the concrete are shown as the sum of the concentrations of the detected 16 EPA PAHs. According to these data the leaching of PAHs occurs constantly from hardening samples. With increasing hardening time from 7 to 91 days the concentration of sum of PAHs in leachates from PF ash concrete increased 9–14 times. In case of CFB ash-based concrete the concentration of PAHs was higher and with increasing hardening time, the concentration increased 1.5 times. However in all cases the concentration of PAHs in leachates was significantly below the threshold limit values of groundwater quality. Hardening of PF and CFB oil shale ash-based concrete does not lead to immobilization of PAHs (Paper VIII).

Table 14. Average pH, EC ($\mu S/cm$) and concentration of individual PAHs ($\mu g/l$) in leachates from oil shale ash-based mortars with respect to hardening time (the value of the SD in parentheses).

| PAHs	PF/1A EF1-3 mortar			CFB/8Amix mortar		
	7 days	28 days	91 days	7 days	28 days	91 days
NA	0.017	0.043	0.038	0.003	0.011	0.004
	(0.003)	(0.009)	(0.008)	(0.001)	(0.002)	(0.001)
AC	nd[*]	nd	nd	0.003	0.003	nd
				(0.001)	(0.001)	
PHN	0.003	0.039	0.012	0.002	0.003	0.007
	(0.001)	(0.008)	(0.002)	(0.0004)	(0.001)	(0.001)
AN	0.024	0.091	0.042	0.005	0.009	0.017
	(0.005)	(0.018)	(0.008)	(0.001)	(0.002)	(0.003)
FL	0.004	0.097	0.029	0.003	0.012	0.011
	(0.001)	(0.019)	(0.006)	(0.001)	(0.002)	(0.002)
PY	0.014	0.101	0.054	0.012	0.013	0.028
	(0.003)	(0.020)	(0.011)	(0.002)	(0.003)	(0.006)
CHR	nd	nd	0.004	nd	nd	0.004
			(0.001)			(0.001)
Sum of PAHs	0.062	0.371	0.179	0.028	0.051	0.071

[*] not detected
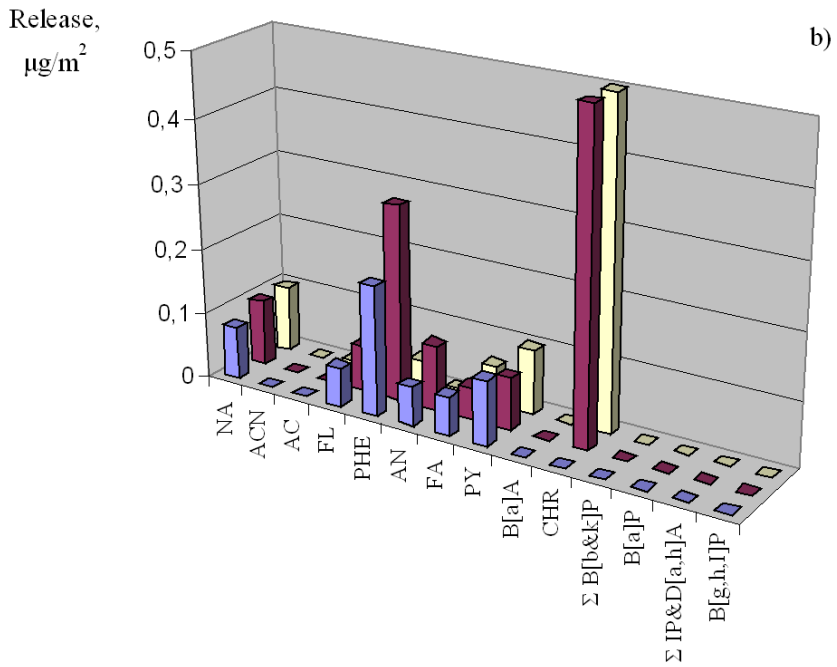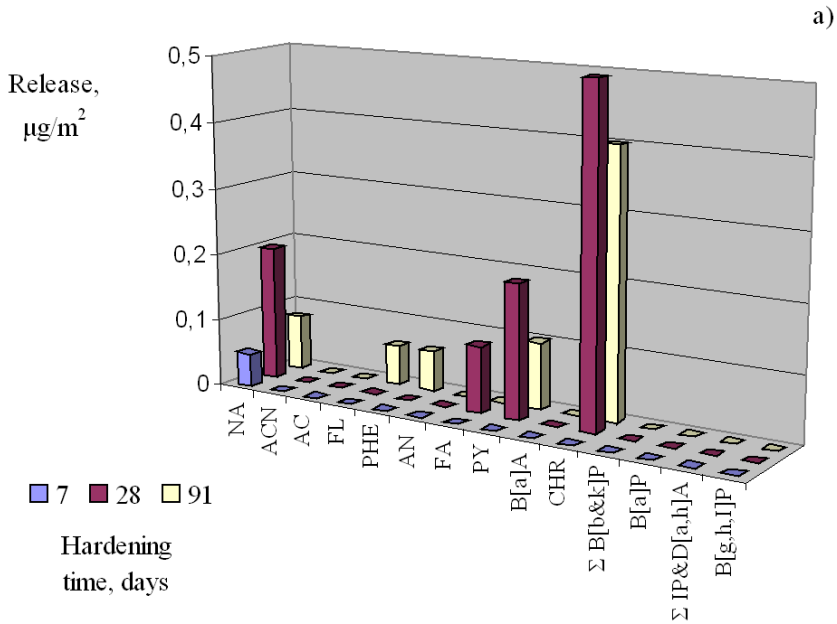
Figure 14. PAH concentration (µg/l) in leachates from a) PF and b) CFB ash-based concrete with respect to hardening time.

5.2.3. Release of metals

Release of elements from oil shale ash samples by leaching test according to the European standard EN 12457-2(2002) (Fig. 1) is presented in Paper VI. Similar or even increased release of several elements as Ca, V, Cr, Ni, Cu, Zn, Mo, Cd, Ba, Tl and Pb was observed in the second extraction cycle of the leaching test compared to the first one which hints that release of these elements from oil shale ash to aqueous phase is a continuous process for a longer period of time. Results reveal that the mobility of most trace elements from oil shale ash is higher in case of PF boiler compared to CFB boiler. After two sequential extraction cycles of leaching test of oil shale ash samples the most mobile element studied was observed to be Sr in selected ashes both in the PF and CFB boiler (Paper VI). In case of the PF boiler particularly high mobility was found for thallium (Tl) compared to ashes of CFB boiler. Among other trace elements relatively high mobility of Mo and Rb was shown for ash samples from both the PF and CFB boilers, followed by Ba and Cu. Relatively high mobility was also observed for the toxic elements Cr, Sn, Cd and Pb, whereas elements such as V, Ni, and Zn were generally low and La, Th and U very low. Obtained results reveal that the release of potentially hazard elements from bottom and fly oil shale ash is significantly lower than the national and EU permissible limits to landfill leachates (Council Decision 2003/33/EC) and the results are similar to literature data (Blinova et al., 2012; Moreno et al., 2005) produced by one-stage compliance leaching tests with similar ash and leaching tests (solid-to-water ratio 1/10 at material's own pH) (Paper VI).

The results indicated that application of oil shale ash in mortars leads to a decrease in readily soluble inorganic components and does not increase the leaching of hazardous Zn and Cd. The concentration of Cd and Zn in all leachates was below the detection limit (Paper VII). In long-term leaching study Cr, Mo and Sr leached through the all time of experiment (142 days). However, the concentration of elements was low: Cr 0.001 – 0.02 mg/l and 0.002 – 0.02 mg/l, Mo 0.002 – 0.05 mg/l and 0.001 – 0.003 mg/l, Sr 0.005 – 0.41 mg/l and 0.007 – 0.25 mg/l for the PF and the CFB oil shale ash-based concrete, respectively. The concentration of Cu and Pb was below the detection limit (0.001 mg/l) (unpublished data). Obtained results indicated difference in leaching behaviour of ash formed under different combustion conditions and composite materials containing same ash fractions probably due to differences in mineralogical composition. Release of elements changed with increase of hardening time. Further study will address these issues.

6. CONCLUSIONS

As oil shale processing wastes contain pollutants it is essential to assess which compounds and amounts could be released to the surrounding environment. Spent shale – the waste from oil shale retorting, oil shale ash – the waste from oil shale combustion and oil shale processing waste-based products were investigated in terms of organic and inorganic pollutant leaching (PAHs and metals). Long-term leaching of PAHs and metals from spent shale under environmental conditions was evaluated. PF and CFB oil shale ash and oil shale ash-based products were subjected to the laboratory leaching test. Main factors that influence on the fate and transport of pollutants were determined. Change of technology in oil shale processing lead to change of waste composition, and thus environmental properties of wastes both from retorting and combustion.

Performed over more than 5 years under environmentally realistic conditions, this study offers an insight into the fate of organic and inorganic pollutants (PAHs and metals) industrial waste deposit. Long-term field leaching is an effective tool to characterize fate and transport of organic and inorganic pollutants from industrial waste deposit. The environmental impact of a solid waste deposit could be evaluated by using a simple and effective low-cost field sampling method. The leaching study was conducted both on the aged and fresh spent shale disposal. It was found out, that industrial spent shale waste deposits could be a source of potentially hazardous compounds like PAHs and metals to the surrounding environment for a long period of time. Results from the present study indicate an increased leachibility of PAHs with time from spent shale deposits, however important to note that their concentrations were low. Distribution, detection frequency of PAHs in fresh and aged waste deposit was different. Among detected PAHs, ACN was detected at the highest concentration, followed by PHE, PY and B[a]A in aged spent shale deposit, PHE showed the highest concentration in fresh spent shale deposit, followed by NA, ACN and PY. The concentrations of elements in field leachates were also determined. The highest concentration of Mo, Zn and Ni were found in leachates from the active part of the deposit. Mo exhibited the highest mobility although its absolute amount in spent shale is relatively small. It was proposed that colloids could be involved in transport of potentially hazardous pollutants. PAHs and metals leaching behaviour depended on the characteristics of the deposited waste, and consequently on technology used for oil shale retorting. Although the concentration of PAHs and heavy metals in field leachates were below permissible limits, the spent shale deposit may represent a constant source of low concentrations of potentially hazardous PAHs and elements, particularly Mo, Ni and Zn.

The demand for enhanced sensitivity and delectability in analytical technologies is great. The use of monofluorinated PAHs (F-PAHs®) as internal standards improved precision of the quantification. The application of F-PAHs as internal standards in GC-MS analysis for PAHs in oil shale wastes was performed at the first time for that sort of matrix. The study revealed that

fluorobenzo[k]fluoranthene could be used as internal standard for quantification of PAHs content in oil shale solid wastes.

Novel passive sampling tool (SPME) was used first time for research of such type of matrix. The SPME technique was optimized for determination of freely dissolved concentration of PAHs in leachates from hazardous waste. SPME technique could be applied for risk assessment of contaminated sites for evaluation of bioavailable fraction (C_{free}) of PAHs. Thus, the method is recommended for analysis of PAHs in complex technogenic matrices. C_{free} is a small fraction of C_{total}, indicating strong association of PAHs with organic and mineral (colloid, clay) matter. Only $0.01 - 2.7\%$ of C_{total} of studied PAHs in the samples comprised for C_{free}.

New method of monolith leaching (CEN/TC 15862, 2012) was applied and performed. Comparative study of the ash-based materials originating from the new CFB and the old PF combustion technology was conducted. The leaching properties of each oil shale ash – based material depended on the specific characteristics of ash and hardening time. Concentration of the sum of PAHs in leachates was higher for PF ash samples if compare with CFB ash samples. The mobility of PAHs from CFB and PF oil shale ash is 20.2% and 9.9%, respectively. Low molecular weight PAHs leached from all mortar and concrete samples, irrespective of hardening period. The concentration of PAHs in all leachates was below the threshold limit values of groundwater quality. Hardening of PF and CFB oil shale ash – based concrete does not lead to immobilization of soluble PAHs. During the experiments no leaching of Cd and Zn from oil shale ash mortars was observed.

The obtained results enlarge our knowledge about the environmental properties of oil shale processing wastes and waste-based materials. The achieved results expand our knowledge about the environmental properties of oil shale ash-based building materials, including backfilling composites for underground mining industry. The methods used in the study could be used for environmental risk assessment of industrial waste and waste-based materials.

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SUMMARY IN ESTONIAN

Polütsüklilste aroomatsete süsivesinikke (PAH-ide) ja raske metallide leostus põlevkivitöötlemise jäätmetest ja põlvekivi jäätmete – põhinevatest produktidest

Tänapäeval on põlevkivi kasutamisel välja töötatud kaks põhisuunda: põlevkivi põletatakse kütusena elektrienergia tootmisel ning termilise töötlemise käigus põlevkiviõli tootmiseks. Põlevkivi põletamisel on kasutusele võetud kaks tehnoloogiat: tolmpõletus ja keevkiht tehnoloogia. Põlevkiviõli tootmisel kasutatakse Kiviter ja Galoter protsessi. Põlevkivi suure mineraalaine sisalduse tõttu tekitatakse töötlemise käigus suurtes kogustes tahkeid jäätmeid: termilise töötlemise käigus tekib põlevkivi poolkoks ja põletamisel tekib põlevkivi tuhk, millest taaskasutatakse ainult väike osa. Vastavalt Euroopa Komisjoni otsusele 2000/532/EC kuuluvad nii põlevkivi põletamisel tekkiv tuhk kui ka termilisel töötlemisel tekkiv poolkoks ohtlike jäätmete hulka. Põlevkivi termilise töötlemise jäätmed on leeliselised ja sisaldavad ohtlikke raskmetalle ja polütsüklilisi aromaatseid süsivesinikke (PAH-e).

Doktoritöö eesmärgiks on põlevkivijäätmete ja põlevkivijäätmetest valmistatud ehitusmaterjalide keskkonnaohtlikkuse hindamine. Jäätmete keskkonnamõju sõltub pigem saasteainete mobiilsusest, mitte nende sisaldusest lähtematerjalis. Seetõttu saab mõju keskkonnale hinnata vaid läbi aine ülekande tahkest faasist vesifaasi, ehk leostumise abil.

Käesolev töö tutvustab leostuvusuuringu meetodit välitingimustel. Selgus, et poolkoksimäed on ohtlikke PAH-ide ja metallide allikaks pika aja jooksul. Uuring näitas võimalust hinnata tahkete jäätmete hoidlate keskkonnamõju tõhusa ning odava meetodiga välitingimustes kasutamiseks. Kuigi PAH-ide ja raskmetallide kontsentratsioon leosvees oli alla lubatud piirväärtusi, on põlevkivi jäätmete hoidla ohtlikke PAH-ide ja raskmetallide, eriti Mo, Ni ja Zn pidev allikas. Mõne leovee proovides leiti PAH-e, mis on liigitatud kantserogeensteks (benso(a)püreen, benso(a)antratseen, benso(k)fluoranteen, benso(b)fluoranteen). PAH-ide leostuvus vanast poolkoksi jäätmehoidlast oli suurem võrreldes hiljuti võetud kasutusele hoidlaga. Töös näidati, et metallide transpordiga keskkonnas võivad olla seotud kolloidid.

Kuna nõudlus analüütiliste tehnoloogiate parema tundlikkuse ja madalamate avastamispiiride järgi on suur, uuriti fluoro-PAH-ide (F-PAH-id) kasutust sisestanarditena GC-MS analüüsil. Selgus, et fluorobenzo(k)fluoranteeni võib soovitada sisestandardiks PAH-ide sisalduse määramiseks põlevkivijäätmetes.

Käesolevas töös uuriti uudse SPME (Solid Phase Microextraction, ehk Tahke Faasi Mikroekstraktsioon) meetodi rakendamist leovee analüüsil. SPME metoodikat saab kasutada bioloogiliselt kättesaadava (C_{free}) PAH-ide fraktsiooni määramiseks. Selgus, et C_{free} on väike osa kogu PAH-idest (ainult 0,01–2,7%) leostusvee proovides, mis näitab PAH-ide tugevat seost orgaaniliste ja mineraalainetega.

Töö eesmärgiks oli hinnata põlevkivituha ja sellest valmistatud ehitusmaterjalide keskkonnaomadusi eriti PAH-ide ja metallide väljaleostumist. Hinnati leostuskäitumist tolmpõletuse ja keevkihtkatla lendtuhast ning tuhast valmistatud mörtidest ja betoonkehadest. Selleks kasutati granuleeritud materjali leostustesti EN 12457-2(2002) ja monoliitse materjali leostustesti EN CEN/TC 15862(2012). Määrati peamised tegurid, mis mõjutavad PAH-ide väljaleostumist tolmpõletuse ja keevkihtkatla lendtuhast ning hinnati tuhast valmistatud mörtide ja betoonkehade tardumisaja mõju PAH-ide väljaleostumisele. PAH-ide sisaldus leovees oli madalam põhjavee keskkonnakvaliteedinäitajatest. Väikese molekulmassiga PAH-ide leostumine leidis aset kõikidest mörtidest ja betoonkehadest, sõltumata tardumisajast. Tööst järeldub, et tardumisaeg ei vähenda vees lahustuvate PAH-ide väljaleostumist tuhast valmistatud mörtidest ja betoonist, kuid sellega seotud keskkonnarisk vesikeskkonnale on minimaalne.

Töö tulemusena saadi väärtusliku infot põlevkivitööstuse tahkete jäätmete ning neist valmistatud produktide käitumise keskkonnas.

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PUBLICATIONS

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2007–2015   University of Tartu – **PhD student** – Faculty of Science and Technology, *"Leaching of polycyclic aromatic hydrocarbons (PAHs) and heavy metals from the oil shale processing wastes and from waste-based products." Supervisors: Uuve Kirso, Toomas Tenno, Natalya Irha*

2005–2007   Tallinn University of Technology – **MSc** – Chemical and Environmental Technology Department *Master thesis: "The Fenton chemistry and its combination with coagulation for treatment of dye solutions." Supervisor M. Trapido*

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Supervisor of Eero Piirisalu *Master thesis* "Leaching behaviour of oil shale ash based composite materials" (2013) University of Tartu

Main scientific publications:

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