DISSERTATIONES TECHNOLOGIAE CIRCUMIECTORUM
UNIVERSITATIS TARTUENSIS

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RIHO MÕTLEP

Composition and diagenesis of oil shale industrial solid wastes

Department of Geology, Institute of Ecology and Earth Sciences, Faculty of Science and Technology, University of Tartu, Estonia.

Dissertation was accepted for the commencement of the degree of *Doctor philosophiae* in geotechnology at the University of Tartu on October 26, 2010 by the Scientific Council on Environmental Technology of the Faculty of Science and Technology, University of Tartu.

Supervisor: Prof. Kalle Kirsimäe, University of Tartu.

Opponent: Prof. Ron Zevenhoven, Åbo Akademi University

Commencement: Room 204, Ülikooli 18, Tartu, on 15 December 2010 at 14.15 p.m.

Publication of this thesis is granted by the Institute of Ecology and Earth Sciences, University of Tartu and by the Doctoral School of Earth Sciences and Ecology created under the auspices of the European Social Fund.

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LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by their Roman numerals. The papers are reprinted by kind permission of the publishers.

I   **Mõtlep, R.**, Kirsimäe, K., Talviste, P., Puura, E., Jürgenson, J. 2007. Mineral composition of Estonian oil shale semi-coke sediments. Oil Shale, 24 (3), 405–422.

II   Bityukova, L., **Mõtlep, R.**, Kirsimäe, K. 2010. Composition of oil shale ashes from pulverized firing and circulating fluidized-bed boiler in Narva Thermal Power Plants, Estonia. Oil Shale, 27 (4), xx–xx. doi: 10.3176/oil.2010.4.??

III   Liira, M., Kirsimäe, K., Kuusik, R., **Mõtlep, R.** 2009. Transformation of calcareous oil-shale circulating fluidized-bed combustion boiler ashes under wet conditions. Fuel, 88 (4), 712–718.

IV   Pihu, T., Arro, H., Prikk, A., Rootamm, R., Konist, A., Kirsimäe, K., Liira, M., **Mõtlep, R.** 2010. Properties and cementation of oil shale CFBC ashes in ash plateaus. Fuel, [submitted, in revision].

V   **Mõtlep, R.**, Sild, T., Puura, E., Kirsimäe, K. 2010. Composition, diagenetic transformation and alkalinity potential of oil shale ash sediments. Journal of Hazardous Materials, 184 (1–3), 567–573.

Author's contribution
Paper I: The author was primarily responsible for planning original research, fieldwork, X-ray diffraction analysis interpretation of analytical data and writing the manuscript.
Paper II: The author was responsible for collection of mineralogical X-ray diffraction and scanning electron microscopy data, interpretation and synthesis of chemical and mineralogical analysis and writing the manuscript (approximately 50%).
Paper III: The author was partly responsible for experiment planning, scanning electron microscopy analysis, interpretation of X-ray diffraction and chemical analysis data and contributed to the writing the manuscript (approximately 30%).
Paper IV: The author's contribution involves X-ray diffraction and scanning electron microscopy analysis, interpretation of the results and writing of the manuscript (approximately 25%).
Paper V: The author's contribution involves data analysis, interpretation of the results and primarily writing the manuscript.

I. INTRODUCTION

Solid fossil fuels (e.g. coal) account for about one-quarter of the world's total primary energy supply. The overall solid fuel consumption is estimated to increase in the coming decades due to the rising energy demand, especially in fast-growing economies (IEA, 2006; Dellantonio, 2010). Combustion of solid fuels leaves, compared to natural gas or oil, a large amount of solid waste posing an increasing threat to air, soil and water quality.

Moreover, the growing global energy demand forces employment of fossil fuels of lower quality like oil shale. According to the World Energy Council, the total world resources of oil shale (expressed as extractable shale-oil) are at least 500 billion tonnes. The mineral matter content of the commercial-grade oil shales varies between 77 and 87 wt% (Puura & Puura, 2007), which is a lot higher than the content of 5–20% in typical coal. Therefore, the large-scale use of oil shale fuels will cause, in addition to emissions of greenhouse gases, technological and environmental problems concerning handling large amounts (hundreds of million tonnes) of combustion waste.

The Estonian kukersite oil shale is the largest industrially exploitable oil shale resource in the world (Teedumäe & Raukas, 2006). Oil shale is the most important natural resource in Estonia and of vital importance in the country's energy sector. About two thirds of Estonia's fuel balance is covered by oil shale and its share in electricity production exceeds 95% (IEA, 2007; Statistical Yearbook of Estonia, 2010). Oil shale mining in Estonia reached its peak in 1980, when 31 million tonnes of oil shale were unearthed. After the commissioning of the Leningrad Nuclear Power Plant in Sosnovy Bor in 1981, the demand for oil shale electricity in the region (Leningrad oblast) decreased and the peak production numbers fell considerably. A decade later the annual oil shale production fell to about 20 Mt and the next decade saw another production drop to about 11 Mt per year. In the last 5 years the annual oil shale mining output has levelled at about 14 to 16 Mt but is estimated to increase slowly (Kattai et al., 2000; Statistical Yearbook of Estonia, 2010). The majority (close to 80%) of mined oil shale is utilized in thermal power plants for electricity and heat production. About 20% is used for retorting shale-oil and shale-gas and the rest is mostly used in cement industry. Oil shale combustion in electric power plants and retorting in oil shale chemical industry for production of shale-oil and combustible gas generate huge amounts of waste – oil shale ash and semi-coke. In electric power plants the ash that remains after combustion makes up 45–48% of the oil shale dry mass (Bauert & Kattai, 1997). The formation of such a large quantity of ash causes difficulties in heat-transfer and phase-separation processes in boilers as well as in transport and deposition of ash (Kuusik et al., 2005). Only a small percentage of ash finds its way to secondary use, either in construction materials, in agriculture for liming acid soils or in road construction as a stabilizing agent of roadbeds. Despite long-time research of reusability options, a vast majority of ash is still deposited on ash sediment plateaus next to the power plants. The amount of ash annually deposited in

waste plateaus ranges between 5 and 7 Mt and the total ash waste volume is close to 300 Mt.

Volumes of waste from oil shale chemical industry are several times smaller, but since this waste contains considerable amounts of residual organics, it is regarded environmentally even more hazardous. The oil shale retorting technologies in operation today produce about 3 t of retorting waste, semi-coke, with each tonne of commercial shale-oil. More than 100 Mt of semi-coke has been deposited since the beginning of oil production in 1921. At the same time semi-coke has even less reusability applications than ash from electric power plants.

Kukersite oil shale is highly calcareous (proportions of calcite and dolomite in oil shale vary between 20 and 70%), and the ash remaining after combustion is due to partial-to-complete thermal decomposition of carbonate minerals, and subsequent reactions with sulphur containing flue gases, rich in lime (CaO_{free}) and anhydrite. As a result, the recycled ash transportation water and waters draining off the ash and semi-coke deposits are highly alkaline (pH 12–13). The highly alkaline leachate of ash sediments poses an environmental risk and the ash plateaus are considered as major pollution sources (Savitskaja, 1997).

Over the past decades oil shale geology and the oil shale combustion and retorting technology have been studied in detail by many researches (see for a review, e.g. Aarna & Lippmaa, 1955; Dilaktorski, 1962; Vingisaar et al., 1984; Koel, 1999; Kattai et al., 2000; Paat, 2002; Golubev, 2003; Lille, 2003; Veiderma, 2003; Soone & Doilov, 2003; Arro et al., 2005; ; Hotta et al., 2005; Ots, 2006; Valdma et al., 2009). However, less attention has been paid to the phase composition and diagenetic transformation of the solid wastes remaining after combustion or retorting. Recent trends in environmental policies and concerns have placed an emphasis on the study of these solid wastes in order to assert the variables that may or may not influence the surrounding environment. In this respect, significant advances have been made in recent years in studies of the CO_2 capture in oil shale ash (Kuusik et al., 2002; Uibu et al., 2008; Trikkel et al., 2010; Velts et al., 2010).

Oil shale industry can roughly be divided into three sections: mining, electricity and heat generation, and chemical industry. Each section has its own unique processing waste(s): mining refuse (mainly limestone with minor oil shale), combustion ash, and retorting residue – semi-coke. This thesis will focus on the last two solid wastes: ash and semi-coke.

The objectives of this dissertation are to:
– characterize the composition of oil shale industry's solid wastes – ash and semi-coke – in fresh unhydrated and hydrated state;
– study the short- and long-term diagenetic transformation and stability of secondary phases in ash and semi-coke deposits;
– establish the alkalinity potential of ash sediments and to understand the technological problems of oil shale ash management after the employment of new technologies in oil shale combustion.

2. OIL SHALE

2.1. Origin and composition of oil shale

Oil shales are fine-grained sedimentary rocks that contain relatively large amounts (10–65%) of organic matter (kerogen) from which shale-oil and combustible gas can be extracted by destructive distillation. Oil shales are found worldwide in all types of marine, lacustrine or terrestrial sedimentary rocks of Cambrian to Neogene age. Organic-rich calcareous sediment – kukersite – found in Lower to Upper Ordovician sediments in Estonia and north-western Russia is a marine oil shale (Bauert & Kattai, 1997). The organic matter of kukersite is composed mostly of kerogen with a few per cent of bitumen (Koel, 1999). Kerogen consists almost entirely of accumulations of discrete bodies, telalginite, derived from a colonial microorganism *Gloeocapsomorpha prisca* (Koel, 1999; Lille et al., 2002). However, Kattai et al. (2000) point out that kukersite kerogen is more similar to lacustrine oil shales and sapropelic coals than to the kerogen of typical marine oil shales.

The major components of organic matrix are phenolic moieties with linear alkyl side-chains (Kahru & Põllumaa, 2006). The elemental composition of oil shale organic matter is characterized by low C/H and C/O ratios, which is common to liquid fuels. The average value of C in oil shale organic matter is 77.5%, O – 10%, H – 9.7% and S – 1.8%. High chlorine content (0.75%) is another notable characteristic. The total moisture content of oil shale burned at power plants is 11–13% and the calorific value is 8–10 MJ kg^{-1}, which is lower than that of the other fuels (average coal – 22.5 MJ kg^{-1}, natural gas – 33.5 MJ m^{-3}, peat briquette – 16.5 MJ kg^{-1}) (Ots, 2006; Valdma et al., 2009).

Besides organic matter, Estonian kukersite contains significant amounts of carbonaceous and terrigenous matter, which constitute kukersite mineral matter. According to the composition, the oil shale mineral part can be divided into a terrigenous or sandy-clay part and a carbonate part. The terrigenous part is closely intertwined with oil shale organic matter and thus can be considered as inherent mineral impurity. Carbonate matter, on the contrary, forms usually separate layers or is arranged as concretions inside and between oil shale seams, and is therefore considered as extraneous mineral matter (Ots, 2006). The chemical and mineralogical composition of carbonate and terrigenous part of oil shale is quite stable, irrespective of the areal location of the deposit or the layer. However, the ratio of terrigenous to carbonate part may vary considerably and is reflected in the fuel quality. The average mineral composition of oil shale is dominated by carbonate minerals (20–70%) including mostly calcite and less dolomite. The proportion of terrigenous fraction is about 15–60%, and that of organic matter varies between 10 and 60% (Bauert & Kattai, 1997; Ots, 2006).

The chemical composition (Table 1) of the oil shale carbonate part is explicitly dominated by CaO (48.1%), followed by MgO (6.6%). The content of CO$_2$ is 45.1% but it is excluded from the calculations of fuel ashing when

proportions of ash in oil shale are considered. The terrigenous part of oil shale mineral matter is dominated by SiO_2, Al_2O_3, Fe_2O_3 and K_2O. It contains a small percentage of crystal water bound to clay mineral phases.

As suggested by the chemical composition, the mineral composition of the oil shale inorganic part is dominated by calcite, dolomite and terrigenous mineral phases (clay minerals, quartz, K-feldspar), and minor pyrite (Table 2). The proportion of terrigenous fraction in oil shale beds varies typically between 20 and 50%, while the proportion of carbonate minerals ranges from 50 and 75% (PAPER II).

Table 1. Chemical composition of oil shale mineral matter, wt% (Arro, 1998).

Terrigenous part, wt%		Carbonate part, wt%	
SiO_2	59.8	CaO	48.1
CaO	0.7	MgO	6.6
Al_2O_3	16.1	FeO	0.2
Fe_2O_3	2.8	CO_2	45.1
TiO_2	0.7		
MgO	0.4		
Na_2O	0.8		
K_2O	6.3		
FeS_2	9.3		
SO_3	0.5		
H_2O	2.6		

Table 2. Mineral composition of oil shale (Lida Bityukova unpublished data 2010) in wt%. The average mineral composition is shown according to Vingisaar et al. (1984); tr. – trace amount, n.d. – not determined.

Sample/Mineral		Kiviõli 1	Kiviõli 2	Viru	Content range
Quartz	SiO_2	12.6	7.8	12.7	4–18
Calcite	$CaCO_3$	36.0	60.4	33.8	30–70
Dolomite	$CaMg(CO_3)_2$	14.7	7.8	17.7	5–30
K-feldspar	$KAlSi_3O_8$	9.1	3.5	9.4	1–2
Albite	$NaAlSi_3O_8$		tr.		n.d.
Chlorite	$Al_2Mg_5Si_3O_{10}(OH)_8$	5.8	2.1	3.3	0–3
Illite	$KAl_2(Si_3AlO_{10})(OH)_2$	14.6	11.1	19.	5–36
Pyrite	FeS_2	6.1	6.9	4.1	n.d.
Gypsum	$CaSO_4 \cdot 2H_2O$	1	tr.		n.d.

Microelement concentrations in oil shale usually do not exceed their respective average concentrations in the earth's crust. The concentrations of Sr, Br and Ba are somewhat higher but in most cases oil shale is not enriched with trace elements (Kattai et al., 2000; Ots, 2006; Table 3).

Table 3. Proportions of selected trace elements in oil shale and the earth's crust, ppm (Kattai et al., 2000; Ots, 2006).

Element	Symbol	Oil shale	Earth's crust
Antimony	Sb	0.5–0.6	0.4
Arsenic	As	7.6–21	50
Barium	Ba	1,150–1,500	650
Mercury	Hg	0.08–0.3	0.08
Cadmium	Cd	0.4–4	0.5
Cobalt	Co	2.9–3	20
Chromium	Cr	17–38	83
Manganese	Mn	310–387	950
Molybdenum	Mo	3	1.5
Nickel	Ni	12–21	60
Lead	Pb	20–30	16
Thorium	Th	2.3–3.4	13
Caesium	Cs	1.7–2.3	3.5
Uranium	U	3	2.8
Copper	Cu	17–55	47
Scandium	Sc	4.2	
Vanadium	V	28	
Zinc	Zn	48.7	
Gallium	Ga	8	
Selene	Se	<0.1	
Bromium	Br	100	
Rubidium	Rb	39	
Yttrium	Y	5.4	
Zircon	Zr	49	
Niobium	Nb	4.5	
Hafnium	Hf	1.8	
Tungsten	W	0.6	

2.2. Oil shale resources and use

Kukersite occurs in an area of about 5000 km^2 in north-eastern Estonia and north-western Russia and forms two large deposits (Figure 1). (1) Estonia-Leningrad deposit is located in north-eastern Estonia and north-western Russia. The productive seam thickness varies from 2.7–3.0 m in the northern part of the deposit where it outcrops to the surface to 1.4–2.0 m in the southern and

western parts where the seam is buried at a 50–90 m depth. (2) Tapa deposit is situated south-west of the Estonia deposit with a seam depth of 60–170 m below the surface. The oil shale seam has a maximum thickness of 2.0–2.3 m in the central part of the deposit. The Tapa deposit is a prospective resource and has not been in use so far (Kattai et al., 2000). The reserves of the Estonia deposits lying in an area of 2973 km^2 make nearly 5x10^9 t, including 1.5x10^9 t of active reserves (Ots, 2006).
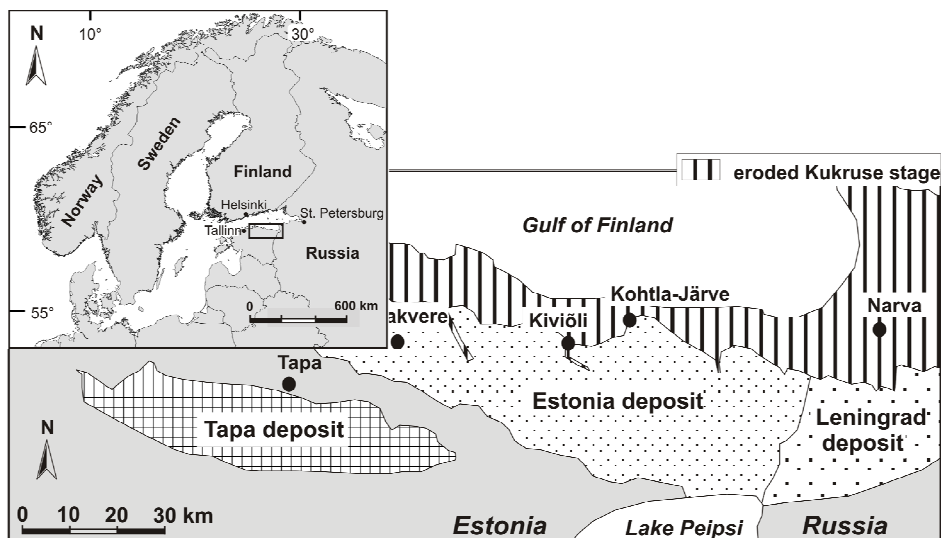
Figure 1. Geological sketch indicating the distribution of the Estonia-Leningrad and Tapa oil shale deposits (after Bauert & Kattai, 1997).

The Ordovician section in North Estonia hosts in addition to kukersite oil shale also Lower Ordovician organic-rich shales known as *Dictyonema shale*. The *Dictyonema shale* occurs in an area of about 11 000 km^2 with the thickness of the seam 1–8 m. Reserves of this shale considerably surpass those of kukersite, but the quality of the shale is poor: heating value 5–8 MJ kg^{-1}, oil yield (Fischer Assay) 3–5%, sulphur content 2–4%. This prevents their utilization for energy production and processing into oil (Koel, 1999).

The Estonia kukersite deposit is the largest oil shale resource in the world used industrially today (Bauert & Kattai, 1997). Oil shales have been known here since the 18th century and large-scale exploration for oil shale deposits and subsequent exploitation started already during World War I. Nowadays the main industrial activities using the oil shale resource are electricity and heat generation and conversion to other forms of fuels (shale-oil, shale-oil gas). Before and during the first years after World War II electricity production was a side-branch in the oil shale consumption, as preference was given to its

processing into oil products and fuel gas. Today oil shale is primarily used for electricity production in two large power plants – the Balti Power Plant (established in 1959) and the Eesti Power Plant (established in 1969).

Since the beginning of the continuous oil shale mining 92 years ago about 1 billion tonnes of oil shale has been mined. The peak annual production (mining) of kukersite was 31 Mt in 1980. The mining of oil shale has decreased since that to 21.1 Mt in 1990 and 12.5 Mt in 1998. In recent years mining has somewhat stabilized at 14–16 Mt (Kattai et al., 2000; Statistical Yearbook of Estonia, 2010).

Oil shale is used as a fuel in five thermal power plants: the Eesti TPP, Balti TPP (together called the Narva TPPs), Ahtme TPP, Kohtla-Järve TPP and Sillamäe TPP. The last three power plants are small-scale, approximately in the range of 20–30 MW, in comparison with the electric/energetic output of the Eesti and Balti TPPs, and their consumption of oil shale feed is many times smaller. Today the two most powerful Estonian thermal power plants use two different oil shale combustion technologies: pulverized firing (PF) and circulating fluidized bed combustion (CFBC) technologies.

Pulverized firing uses pulverized oil shale (median size 45–55 μm) that is fed into the combustion chamber by hot air as a transporting medium and mixed there with hot secondary air. During the combustion heat is released and transferred through heat transfer surfaces to water (steam). At the same time various conversion processes with fuel mineral matter occur, and ash is formed. The combustion temperature inside the furnace is about 1350–1450 °C and can reach 1500 °C (Ots, 2006).

Pulverized firing boilers have six ash collection sections: furnace, superheater, economizer, air-preheater, cyclones and electrostatic precipitators (Figure 2). The ash is transported to the ash plateaus by the hydraulic ash removal system through water pipes as a water slurry at an ash to water ratio of 1:20. The ash that is finally deposited on ash disposal sites or plateaus (hereafter called ash plateaus) is a mixture of ash of different particle sizes from different ash separation system sections.

More than 95% of the ash produced in oil shale combustion (approximately 6–7 Mt annually) is transported to the ash plateaus and stays there for an indefinite period. Over the past decades substantial research has been conducted for finding suitable ways for utilizing ash, but no good solutions have been achieved so far. In the 1970s–80s oil shale ash was intensively used in road construction as a stabilizing agent of road beds (Paat, 2002). Large amounts of ash have been used for the production of construction materials (e.g. gas-concrete) and ash has been used as an additive in Portland cement production (Hanni, 1996). Ash has also been a valuable soil liming agent in agriculture (Pets et al., 1985). Recent studies have shown that ash sediments can be used as an effective filter material for wastewater treatment (e.g. Vohla et al., 2005; Kaasik et al., 2008; Kõiv et al., 2010). However, the secondary use of ash is very limited and makes up less than 5% of its annual production.
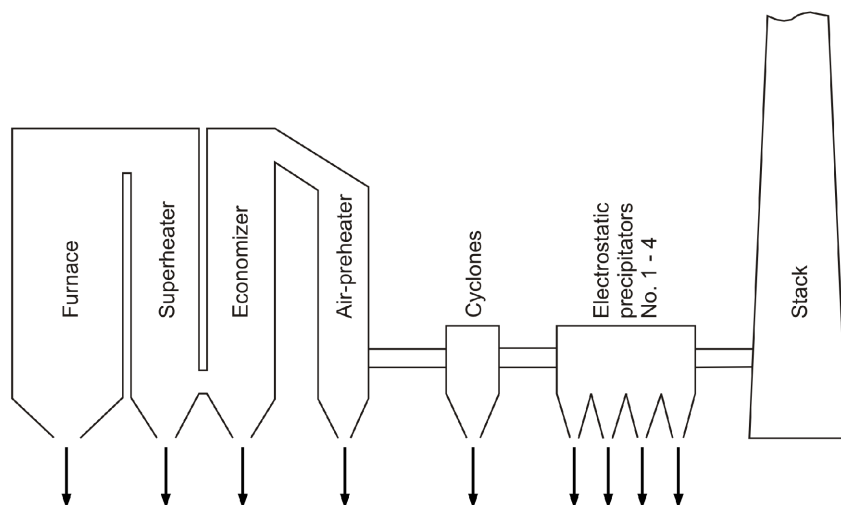
Figure 2. The scheme of PF technology ash removal at the Narva TPPs (after Ots, 2006).

In 2004 the old PF boilers in unit No. 11 in the Balti TPP and unit No. 8 in the Eesti TPP were replaced by new CFBC boilers with the maximal power output of 215 MW. In a more effective and environmentally friendly CFBC boiler the flue gas superficial velocity exceeds gravitational force; particles leave the bed and are transported by rising flue gas to the separator, where most of the particles are captured and returned to the bed, and continuous circulation of the solid phase takes place (Ots, 2006).

Circulating fluidized bed combustion is a low-temperature combustion technology where temperatures are in the range of 750–950 °C. No high temperatures are needed if fuel is fed into a furnace where the temperature in the combustion bed is equal to or slightly higher than the fuel ignition temperature that supports continuous combustion. A lower combustion temperature, compared to PF combustion, favours SO_2 capture, which is almost complete. At a lower combustion temperature CaO_{free} reacts more readily with SO_2 forming a solid $CaSO_4$ (anhydrite) phase. According to the Development Plan of the Estonian Electricity Sector until 2018 (Development plan ..., 2009), the boilers using the PF technology will be partly shut down, partly replaced with CFBC boilers, and four power units will be fitted with sulphur and nitrogen (oxides) capture systems by 2018, for higher efficiency and substantial fuel saving (Liiv, 2007) in the CFBC boilers and significant reducing of air pollution (Liblik et al., 2006).

About 19% of kukersite is used for retorting shale-oil and shale-gas. During oil shale retorting the shale is heated in the absence of oxygen to the temperature at which kerogen is decomposed or pyrolysed into gas, condensable oil and solid residue. The inorganic mineral matrix of the shale is retained in the

form of spent shale (Koel, 1999). Thermal destruction of kukersite begins at 170–180 °C and pyrogenous water appears at 270–290 °C. At temperatures of 350–400 °C the organic substance of kukersite is converted into semi-liquid material, called thermobitumen (Kann et al., 2004). The rate of kerogen (thermobitumen) decomposition is the highest at retort temperatures of 480–520 °C at which kerogen converts into three organic fractions: oil, gas and residual carbon.

Over the past three decades two main methods have been used for producing shale-oil, namely the Kiviter process and the Galoter (solid heat carrier) process. The Kiviter process is conducted in a vertical gas generator, which is internally heated by combustion of coke residue and non-condensable shale gas. Operation of the Kiviter retort is continuous, whereas heat is provided by the rising gases, supplemented by recycle gas and burned in the heat carrier preparation chamber. Additional recycle gas and air are admitted to the chambers near the 900 °C point and heat the shale residue to burn off the coke at the last stage of retorting (Soone & Doilov, 2003). The Kiviter process is suitable for retorting high-calorific (>11 MJ kg^{-1}) oil shale, and oil yield is 15–17% from oil shale. The main drawbacks of the Kiviter process are (1) low energy efficiency, (2) need for concentrated feed of oil shale, (3) formation of potentially hazardous solid retort residue (semi-coke) as a by-product due to incompletely retorted organic matter (up to 30% of organic matter gets lost with semi-coke; Veiderma, 2003).

The Galoter retort uses spent shale as a heat carrier. The process is based on introducing dried oil shale (<25 mm particle size) into an aerofountain drier where it is mixed with hot (590–650 °C) shale ash produced by combustion of oil shale semi-coke (at 740–810 °C at oxygen deficiency) (Golubev, 2003). The oil yield is 11.5–13% in the Galoter process, which is 3–5% less than in the Kiviter process (Veiderma, 2003), but advantages of the Galoter process are as follows: (1) its solid residue (ash) is less harmful to environment, (2) the concentration of organic substances is below 1%, (3) unriched oil shale of lower calorific value can be used.

Since the Kiviter retort cannot accept fines below 25 mm but the Galoter retort requires fines smaller than 25 mm, the two retorts complement each other for full resource utilization (Koel, 1999).

At present oil shale thermal processing plants are located in Kohtla-Järve (*VKG AS*), in Kiviõli (*Kiviõli Keemiatööstuse OÜ*) and on the territory of the Eesti TPP (*Eesti Energia Õlitööstus AS*). Different technologies are employed in those processing plants. The Kiviõli and Kohtla-Järve oil shale processing plants are equipped with vertical retorts or Kiviter technology, *Eesti Energia Õlitööstus AS* uses a solid heat carrier or Galoter (now called Enefit-140) technology. Thermal processing wastes from these two technologies are different. Waste from the Kiviter technology is semi-coke, which is a solid material, black in colour, rich in organic residue and with a specific smell. The Galoter technology produces waste that is essentially similar to oil shale combustion waste and is called black ash. In this study focus is placed on semi-coke from

the Kohtla-Järve thermal processing plant. The Kiviõli processing plant employs the same technology as is used in *VKG AS* and the waste is of the same origin and composition.

For decades from the 1950s on semi-coke was mostly used in the manufacture of mineral wool and to a smaller extent in cement and compost production. Total mineral wool production was ~5.3 million m^3 in 1959–1985, and the estimated share of total semi-coke in feed was 830 thousand t (Veski, 2005). Recently a small amount of semi-coke has been used as an ingredient of composts (approx. 50%) in mixture with pig slurry and peat, and for manufacturing rock wool and IVU blocks. Minor amounts of semi-coke (10 000 t annually) have been used for cement production by the company *Kunda Nordic Cement Ltd*.

3. MATERIAL AND METHODS

3.1. Semi-coke

The studied semi-coke samples were collected at the semi-coke waste deposit plateau of the company *VKG AS* in Kohtla-Järve (figure 1 in PAPER I). The plateau is a central flat area on the waste depository, where semi-coke is deposited today. Mineralogical analysis were performed on fresh semi-coke, waste plateau surface sediments and on samples from six drill cores (P1–P6) from a depth range 0.8–14.7 m. Altogether 47 samples were investigated. The properties of the semi-coke materials were analysed by means of the X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods, which are described in subchapter 3.5.

3.2. Composition of pulverized firing and circulating fluidized bed boiler oil shale ash

The ash samples were collected from different points of the ash separation systems of CFBC and PF boilers in the Balti and Eesti TPPs. The ash samples from the PF boiler in the Balti TPP were taken at the superheater, economizer and four electrostatic precipitator fields. In the Eesti TPP, PF ash was collected at the furnace, superheater, economizer, cyclone separators and three electrostatic precipitator fields (No.1–3). The ash samples from CFBC boilers in the Eesti TPP were collected from the furnace, INTREX superheater, air-preheater, and four electrostatic precipitator fields. In the Balti TPP, in addition to the aforementioned ash samples from the CFBC system of the Eesti TPP, samples were collected from the superheater and economizer (table 1 in PAPER II). Properties of the ash were analysed by means of the XRD, SEM and inductively coupled plasma spectroscopy (ICP-OES, ICP-MS) methods, which are described in subchapter 3.5.

3.3. Hydration and experimental deposition of circulating fluidized bed boiler oil shale ash

The material investigated in PAPER III represents ash material collected from three different parts of the ash separation system of CFBC boilers in the Estonian TPP:
(1) electrostatic precipitator ash from the first field (EP1);
(2) INTREX superheater ash (INT), from the INTREX^{TM} heat exchanger system;

(3) mixture of ash (MIX) from different boiler zones, which represents the average material deposited on ash waste plateaus.

The INTREX^{TM} unit is a steam-cooled heat exchanger, located close to the lower part of the combustion chamber. Solids coming down from the separator of solids (cyclone) are led through the heat exchanger on their way back to the combustion bed of the furnace. Part of the returning ash is separated from INTREX^{TM}. For a more detailed description of INTREX^{TM} see Hotta et al. (2005).

The hydration experiment was carried out in open air containers, where samples were held in fully water saturated state for 1 year. Samples were periodically mixed between and during sampling to prevent the differences caused by slow diffusion effects. Sub-samples were taken at the intervals of 24 h, 3 days, 6 days, 11 days, 19 days, 25 days, 58 days and finally 1 year of hydration. To prevent further hydration and mineral transformation, samples were immediately dried in a vacuum chamber and stored airtight prior to measurements. Properties of hydrated ash were analysed by means of the XRD, SEM and ICP-ES/ICP-MS methods, which are described in subchapter 3.5.

Cementation and the chemical, mineralogical and geotechnical properties of CFBC ash were investigated in the experimental deposition channel on the central dam of the ash plateau at the Balti TPP. The ash slurry was derived from the CFBC energy unit. The length of the channel was ~1000 m and width ~40 m. The channel was filled with ash slurry in autumn 2008. The average flow velocity of ash slurry was in the range 0.2–1.0 m s^{-1}. The surface of the channel was open to the atmosphere and therefore impacted by precipitation/evaporation and freezing/thawing. After ash deposition, excess water was drained, leaving ash sediments exposed to atmospheric conditions. The scheme of the experimental channel and the sampling points are indicated in figure 1 in PAPER IV. The deposited ash material was sampled in four different periods: 2 weeks, 3 months, 5.5 months and 10 months after filling. The first two sampling sessions were carried out with a manual drill, in the last two sessions the samples were taken from the excavation walls. Four trenches ~1 m wide, 5 m long and 0.9–1.5 m deep were made.

Properties of the ash sediments were analysed by means of the chemical silicate analysis, XRD and SEM methods. The uniaxial (compressive) strength, leachability and hydraulic permeability of ash sediments were determined. The *in situ* loading tests for the bearing capacity of the ash deposit were performed during the third sampling session (5.5 months) by using a falling weight device, FWD 8002 (Dynatest, Denmark).

3.4. Composition and diagenesis
of hydrated ash plateau sediments

The material investigated represents the ash plateau sediments sampled at the Eesti TPP. The drill core samples were obtained from geotechnical drillings in the northern part of the plateau, reaching a maximum depth at 33.7 m from the top of the plateau. Only partial coring was conducted, and the samples from different cores were used for a composite depth profile. Altogether 14 samples from seven drill cores were investigated (figure 1 in PAPER V). In addition to core samples, six samples of fresh ash fractions (fly- and furnace/slag ash) of the pulverized firing furnace of the Eesti TPP were investigated for minera-logical composition. Only PF ash was selected because the CFBC firing was introduced in the Eesti TPP only in 2004, and most of the plateau sediments are composed of PF ash. Properties of the ash materials were analysed by means of the XRD, and SEM methods, which are described in subchapter 3.5.

Alkalinity potential of oil shale ash sediments was calculated according to the empirical function presented by Hjelmar (1990) and Kim (2006):

$$ALK = 97(Ca_{NS}) + 175, \tag{1}$$

where
ALK – alkalinity, $meq_{NaOH} \, g^{-1}$
Ca_{NS} – non-silicate calcium, $meq \, g^{-1}$

The neutralization volume of plateau sediments as a function of Ca was found according to Kim (2006):

$$V_N = (0.032Ca–0.09)/N, \tag{2}$$

where
V_N – neutralization volume, $L \, kg^{-1}$
Ca – Ca concentration, $g \, kg^{-1}$
N – normality of the acid, $eq \, L^{-1}$

3.5. Analytical methods

3.5.1. X-ray diffractometry

The mineralogical composition of the studied semi-coke and ash samples was determined by using the Rietveld technique of X-ray diffraction (XRD) ana-lysis. Ground and homogenized randomly oriented powder samples were mea-sured on a Dron 3M diffractometer, using Ni-filtered Cu*K*a radiation over the 2–50 °2θ region, a scan step of 0.02 °2θ and a count time of 5 s per step, and on a Bruker D8 diffractometer, using Ni-filtered Cu*K*a radiation over 2–70 °2θ region, a scan step of 0.02 °2θ and a count time of 2 s per step.

Quantitative mineral composition was determined by full-profile Rietveld analysis with the SIROQUANT™ software system (Taylor, 1991; Ward et al., 2001). The full profile XRD pattern Rietveld method takes into account the integrated intensities of the particular diffractogram peaks and compares natural and artificial mixtures along the whole length of the diffractogram, thus providing considerably more information for mineral quantification (Ward et al., 2001). Allowance was made in the SIROQUANT™ analysis for preferred orientation in several minerals, such as carbonates, whereas a match was obtained for the key peak positions, but the distribution of peak heights was inconsistent with the standard mineral pattern. The standard patterns for such minerals were refined by SIROQUANT™ using computations based on the March-Dollase function preferred orientation correction (Dollase, 1986) and the mineral percentages adjusted accordingly (Ward et al., 2001). For some of the minerals indicated by SIROQUANT™ to be present in low concentrations (<1%) the estimated error is of similar magnitude to, if not greater than, the actual determination. These minerals are considered as traces and were not taken into account when the remaining components were normalized to 100%.

The portion of non-diffracting amorphous (glass-like) phases was estimated from their mass-adsorption effect on the pattern with an added spike of a known phase (halite – NaCl). A mass-adsorption coefficient of silicate composition glass was assumed for the amorphous phases. The accuracy of the amorphous phase determination is not better than 20%.

3.5.2. Scanning electron microscopy

Micromorphology and spatial relationships of secondary mineralization were studied with a Zeiss DSM 940 scanning electron microscope (SEM), equipped with an Idfix Si-drift technology energy-dispersive analyser (EDS), and a Zeiss EVO MA 15 SEM instrument. Depending on the material characteristics and analytical needs, the preparations were coated with conductive gold or carbon prior to analysis in SEM. The mineral phases were identified against the characteristic EDS spectra and morphology of crystallites.

3.5.3. Chemical analysis

The chemical composition of the studied sediments and ash types from the Balti TPP and Eesti TPP were determined with standard inductively coupled plasma spectroscopy (ICP-ES, ICP-MS) techniques at ACME Analytical Laboratories Ltd., Vancouver, Canada.

4. RESULTS AND DISCUSSION

4.1. Composition and diagenesis of semi-coke

The solid retort residue in the Kiviter process, semi-coke, is formed by the transformation of oil shale as a result of its partial thermal decomposition in two stages:

(1) semi-coking process at temperatures 400–520 °C, and

(2) short heating at 900–1000 °C during the final stage of retorting, this is primarily aimed to burn off the coke (organic) residue.

Fresh unhydrated semi-coke. The predominant phases identified by XRD in a fresh unhydrated semi-coke (table 1 and figure 2 in PAPER I) were calcite ($Ca(CO)_3$), dolomite ($CaMg(CO)_3$), quartz (SiO_2), K-feldspar ($KAlSi_3O_8$) and clay minerals (mostly illite – $KAl_2(Si_3AlO_{10})(OH)_2$), which are also the main constituents of oil shale mineral matter. The changes in mineral matter during the first stage of the retorting process, which occurs at air deficiency conditions, are negligible. The terrigenous fractions of oil shale – quartz and feldspars – remain practically unchanged and only clay minerals start to dehydrate. Nevertheless, at these temperatures (400–500 °C) various sulphur compounds (mainly in the form of pyrite and/or marcasite – FeS_2) start to decompose. The sulphur released by pyrite decomposition and the CaO released from partial pyrolysis of calcium carbonate react and form a CaS (oldhamite) type phase (up to 3%), whereas the uncompleted pyrite decomposition process may produce a mackinawite (FeS) type phase, whose traces were found by XRD analysis. In addition to these minerals, fresh semi-coke contains secondary phases formed by partial thermal decomposition and subsequent reactions of carbonate and clay minerals – melilite ($(Ca,Na)_2(Al,Mg,Fe)(Si,Al)_2O_7$), periclase (MgO), clinker-minerals: β-C2S/belite (β-Ca_2SiO_4), merwinite ($Ca_3Mg(SiO_4)_2$). The diffuse maximum from amorphous phase scattering in the measured XRD diffractogram indicates the quantity of non-crystallized matter to be as high as 10(20)%.

The greatest difference of fresh semi-coke from oil shale combustion ash (e.g. PAPER II) is its very low content of lime (CaO_{free}), and its hydration product portlandite ($Ca(OH)_2$) and anhydrite ($CaSO_4$)

Semi-coke is a complex mixture, consisting of thermally degraded matter and pieces of macroscopically unaltered oil shale with only slight signs of thermal decomposition. In addition, a considerable amount of residual organics (about 10%) can be found in semi-coke. Occasionally, semi-coke contains pieces of partly altered carbonate rock together with yellowish-green lumps of partially melted slag, which are composed of amorphous glass phase and high-temperature Ca–Mg silicates – diopside, enstatite and various clinker-minerals (β-C2S, C3S (Ca_3SiO_5), merwinite and traces of Ca-ferrites). These high-temperature phases can result from partial melting of the shale in the

environment created during the final stage of retorting when temperatures of 900–1000 °C are applied to burn off the organic matter/coke in solid residue. However, some mineral phases (e.g. diopside and enstatite) indicate that temperatures as high as 1400–1500 °C can occur locally during this stage. This slag-like material forms at the expense of the decomposition and melting of alumosilicate minerals (clays) and newly formed Ca-silicates – melilite, cement minerals like β-C2S, merwinite, etc. These phases form in reactions between free Ca and Mg oxides derived from the decomposition of dolomite (at ~860 °C) and calcite (at ~950 °C) with alumosilicates (mainly clay minerals and K-feldspar) and less quartz (PAPER I).

Hydrated semi-coke and plateau deposits. The most notable difference between the fresh and deposited semi-coke is the disappearance of oldhamite and the occurrence of a large amount of ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) (11% on average). The average abundance of minerals fluctuates to some degree, probably due to variations in the original deposited sediments and their later alteration. However, certain variations can be observed in drill core samples from various locations and depths. The dominant phases in samples (drill cores P1–P6) are calcite and dolomite; quartz, feldspars (K-feldspar and in trace amounts of albite), clay minerals (illite/illite-smectite); and ettringite (figure 3 in PAPER I). Interestingly, the proportion of ettringite rises slightly with the increasing depth of sampling. However, the increase is not expressed very clearly, and the variation is considerable (figure 4 in PAPER I). There is also a small but consistent increase in ettringite along the profile from the uppermost drill core P1 to the lowermost drill cores P5 and P6 (figure 5 in PAPER I).

The inner variability of the semi-coke waste deposit is probably due to both physical and chemical separation during the deposition of the sediment, and due to different diagenetic/hydration processes. The surface layers of the semi-coke waste heaps are under constant influence of percolating precipitation water, which markedly lowers the pH of pore-water in the upper layers and initiates the dissolution of ettringite. The studied sections indicate that, although not well expressed in all sequences, the ettringite dissolution profile can be traced to a depth of several meters. Also, the notably higher proportions of calcite and dolomite in samples from the drill core (P1) located on the foot of the semi-coke waste heap (figure 3 in PAPER I) can be explained by the gravitational separation during the dumping of the material. The material deposited on the studied area was dumped in large mounds. By dumping, the waste material fractionates gravitationally with the largest particles being transported onto the foot area of the mound (Puura & Pihlak, 1998). The largest particles in semi-coke are usually partially decomposed harder lumps of oil shale and especially carbonate rocks, which are also reflected in the mineral composition of the sediment.

Ettringite acts as the most important cement mineral binding waste particles and therefore stabilizing semi-coke dumps geotechnically. It has also been shown that ettringite formation controls the activity of several contaminants,

both cations and oxoanions, and is concomitant with the reduction of leachate trace elements (Fowler et al., 1993).

Ettringite in semi-coke sediments is formed as a result of the reaction of Ca-phases, formed at the thermal decomposition of limestone/dolomite, with Al-compounds derived from the residual dehydroxylated aluminosilicate clays and/or Al-Si glasses, and with the dissolved sulphur compounds and/or CaS (emitted in the combustion process of organic matter or decomposition product of pyrite and carbonate phases, respectively). In oil shale ash plateau sediments consisting mainly of PF ash, ettringite formation is limited by sulphate deficiency (PAPER V), whereas in semi-coke sediments the controlling factor seems to be the availability of CaO[Ca(OH)$_2$]. It is probable that in semi-coke sediments in the presence of high sulphate activity all free Ca ions will be bound to form ettringite. In semi-coke sediments secondary ettringite typically occurs as 2–10 µm long prismatic crystals that form irregular aggregates in semi-coke open pores (figure 6d,e in PAPER I).

The crucial factor for the formation and stability of ettringite, and therefore the geotechnical stability of semi-coke waste deposit, is the pH of the environment. In alkali and sulphate-rich solutions ettringite is the most stable phase of the $Ca(OH)_2$–$Al_2(SO_4)_3$–H_2O system. Ettringite is stable at pH values >10.7, at lower pH values ettringite dissolves incongruently to gypsum ($CaSO_4 \cdot 2H_2O$), (amorphous) Al-hydroxide and Ca-aluminate type phases (Myneni et al., 1998). However, at high CO_2 partial pressure and a relatively low pH level, ettringite decomposes into sulphates and aragonite ($CaCO_3$) with vaterite (γ-$CaCO_3$) as an intermediate phase (Nishikawa et al., 1992). It is evident that under open atmospheric conditions (e.g. percolating precipitation water) the pH is not retained in the ettringite stability region and the phase becomes decomposed. This is observed in some surface samples of the semi-coke waste deposits where SEM analysis reveals dissolution of ettringite crystallites (figure 6f in PAPER I).

4.2. Composition of pulverized firing and circulating fluidized bed boiler oil shale ash

Different combustion conditions in the PF and CFBC technologies cause remarkable differences in the phase as well as chemical composition of ash fractions (e.g. Kuusik et al., 2005). Different compositions of ash fractions have significant influence on the behaviour of ash under wet deposition (PAPER III), and this can also affect the potential application of ash as a secondary raw material. Different hydration properties of CFBC and PF ash have already caused technological difficulties of ash deposition in waste landfills at thermal power plants (PAPER IV). In earlier decades, PF ash has been extensively studied, while the composition of CFBC ash is virtually unexplored (except Kuusik et al., 2005). Therefore, detailed parallel study of PF and CFBC ash was undertaken in the Eesti and Balti TPPs in order to determine the distribution of mineral and chemical components in different ash fractions.

The chemical composition of all ash types is dominated by CaO, whose proportion varies within 26.4–54.5% in PF ash and 26.4–49.1% in CFBC ash (PAPER II). The content of CaO along the boiler gas pass decreases both in PF and CFBC boiler ash, from 49.4% in furnace ash to 29.7% in the last fields of the electrostatic precipitators (average values). Interestingly, the proportion of MgO (average 4.75%) is much lower than 7–15%, as reported in earlier studies (e.g. Kuusik et al., 2005). Mg is mostly derived from the thermal decomposition of dolomite $(CaMg(CO_3)_2)$ and the difference is evidently due to variation in dolomite admixture in raw oil shale, depending on the geological section used for mining. The separation of S along the boiler gas pass in PF ash types shows gradual enrichment in finer ash fractions, whereas, as expected, in CFBC boilers the S proportion is the highest in the ash removed in the INTREX superheater zone (Kuusik et al., 2005; PAPER II).

Variation in the mineral composition of ash fractions is dominated by lime, ranging from about 1.6% in CFBC ash to a maximum of 24.6% in PF ash. Concordant to the chemical composition of the samples, the proportion of lime in PF ash types at both power stations shows gradual decrease from the furnace ash to the electrostatic precipitators. In CFBC ash, however, the distribution of lime is more complex (figure 4 in PAPER II). The proportion of lime in furnace ash is low compared to PF boilers; it reaches a maximum in the economizer–air-preheater zone, and then decreases again through the fields of electrostatic precipitators. This variation is evidently related to the active sulphur binding after INTREX superheaters, where lime, formed during the thermal decomposition of calcite and dolomite, reacts with SO_2 in flue gases. In contrast to lime, the content of anhydrite increases in PF boilers from about 5% in furnace ash to ~13% and ~27% in electrostatic precipitators at the Balti TPP and Eesti TPP, respectively.

There is a significant difference in the composition of major secondary Ca-silicate phases in ash formed in the Eesti and Balti TPPs. In the Balti TPP Ca-silicates are represented by β-C2S, merwinite and wollastonite $(CaSiO_3)$ type phases. The Ca-silicate composition of the ash types produced in the Eesti TPP, however, includes also C3S and rankinite $(Ca_3Si_2O_7)$ type phases. The difference is also evident in the appearance of akermanite $(Ca_2MgSi_2O_7)$ and C4AF/brownmillerite $(Ca_2(Al,Fe^{3+})_2O_5)$ in all ash types of the Eesti TPP (table 2 in PAPER II). Also, while in PF boilers the proportions of Ca-silicate phases decrease along the boiler gas pass, in the CFBC boiler system, on the contrary, the quantity of Ca-silicates is rather uniform in the first part of the ash removal system, increasing nearly exponentially in the electrostatic precipitators (figure 6 in PAPER II).

This variation between PF and CFBC ash is evidently controlled by firing temperature differences between combustion technologies, and by grain size differences of oil shale fuel. The PF technology exploits high-temperature combustion where the nominal burning temperature inside the furnace chamber reaches 1350–1450 °C (up to 1500 °C), whereas in CFBC the optimum temperature in the furnace chamber is about 850 °C (Ots, 2006). The high temperature

in the PF technology ensures major decomposition of carbonate mineral phases (dolomite, calcite) and melting of clay minerals that form a source for reactive silica as well as aluminium, which control the formation of secondary Ca-silicate and Ca–Al-silicate phases. The firing temperature in CFBC boilers allows thermal decomposition of dolomite, but only partially affects calcite and clay mineral phases. As a consequence, PF ash types are enriched with respect to CaO_{free} and secondary Ca-silicate phases, but CFBC ash types have a higher percentage of residual mineral phases. A specific characteristic of CFBC ash types is the higher concentration of sulphur, mainly in the form of anhydrite ($CaSO_4$) in the INTREX ash.

Separation of the phases (either secondary or residual) along the boiler gas pass depends mainly on the particle size of phases, which is different, depending on the firing technology. Secondary Ca-silicates, produced at high-temperature conditions in the PF boiler, form large (partially inter-melted) aggregates, which are concentrated in coarse ash fractions and are removed in the first zones of the ash removal system. In contrast, at lower firing temperatures, in CBFC boilers, the secondary Ca-silicate phases exist in the form of discrete and fine particles that are preferentially removed in the electrostatic precipitators. At the same time, the anhydrite particles in PF ash have a finer grain size and occur mostly in the ash separated in electrostatic precipitators. In CFBC boilers anhydrite is mostly precipitated in the form of a shell on unreacted CaO_{free} cores (Trikkel et al., 2000; Anthony & Granatstein, 2001), thus forming relatively large particles. As a result, anhydrite is mostly found in the first part of the boiler gas pass (in INTREX ash), and to a lesser degree in adjacent zones (PAPER II).

Our study revealed marked differences between the ash formed in the Eesti and Balti TPPs. The differences in ash composition are particularly well seen in the composition of Ca-silicate phases. In the Balti TPP, secondary Ca-silicates are represented mainly by β-C2S, merwinite and wollastonite, while in the Eesti TPP also C3S, rankinite, as well as C4AF and akermanite are found.

The systematic difference in the composition of secondary Ca-bearing phases, which is evident both in PF and CFBC ash of the Eesti and Balti TPPs, suggests that this variation is caused by the composition/quality of the oil shale fuel used in boilers, not by the technological differences. The Eesti TPP is fed with oil shale, mostly derived from the underground Estonia mine in the central part of the Estonia deposit of the oil shale basin. The Balti TPP, on the other hand, uses oil shale, which is mainly extracted by open-cast mining from Narva quarry in the easternmost part of the deposit. Vingisaar et al. (1984) indicate that the dolomite content in the carbonate fraction of oil shale is somewhat higher in the northern part of the central field and also in the eastern area. The average proportion of MgO in the western part of the Estonia deposit is 2.6% in oil shale beds and 1% in carbonate rock intercalations whereas in the eastern part of the deposit the respective value is 3.9% in oil shale beds and 2.5% in carbonate rock. Dolomite thermal dissociation occurs at a lower temperature than that of calcite, and its higher proportion in oil shale fuel would enhance the

reactions between reactive CaO_{free} and silicate phases, causing compositional variations in Ca-silicate and Ca-silicate-aluminate phases in the Balti and Eesti TPPs (PAPER II). Nevertheless, the proportion of MgO, which is the direct product of dolomite thermal dissociation, is statistically not higher in ash from the Balti TPP, and further studies are needed for the confirmation and understanding of this phenomenon.

4.3. Hydration and experimental deposition of circulating fluidized bed boiler oil shale ash

The much lower combustion temperature (800–850 °C against 1350–1450 °C in PF boilers) and the enhanced phase separation in the CFBC units result in significantly different chemical, physical and phase compositions of CFBC ash compared to PF ash (Kuusik et al., 2005; PAPER II). Most notably CFBC ash contains less lime and Ca-silicate phases (e.g. β-C2S), but is richer in anhydrite. This feature suggests different hydration processes and different cementitious/pozzolanic properties of CFBC oil shale ash as compared to PF ash.

Laboratory scale hydration experiments of CFBC ash (PAPER III) suggest rapid initial hydration reactions during the first 72 hours, governed by lime to portlandite reaction, and anhydrite and periclase dissolution, which was followed by the formation of ettringite after 144 hours in open atmospheric conditions. Significant carbonation of portlandite was observed already during the early phases of the processes, and calcite replaced portlandite almost completely during the first two months of the experiment. After 1 year the mineral composition of hydrated ash was dominated by calcite (44%), whereas the proportion of ettringite in hydrated ash mixture had decreased from 36.5% to only 4.3% after 2 months from the beginning of the experiment. The dissolution of ettringite was accompanied by the appearance of bassanite (9.3%) and gypsum that have consumed the released sulphate and calcium in their formation reactions, while part of the calcium was used for the precipitation of additional calcite. We also noticed that the content of Ca-silicate (β-C2S) had decreased, due to β-C2S reaction with CO_2, resulting in the formation of additional calcite and quartz.

These reactions indicate that the first stage of the CFBC ash hydration process is governed by fast and direct hydration of lime to portlandite (3).

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad\qquad (3)$$
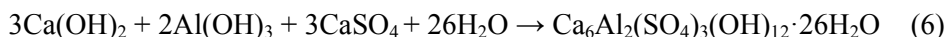
Conversion from lime to portlandite takes place in 24 hours. This agrees with the result of hydration experiment of oil shale PF ash by Kuusik et al. (2004) indicating an almost complete slacking of lime during the first 24 hours of reaction in open containers. However, as noted by Anthony et al. (2005), the hydration of CFBC ash is somewhat slower as compared to the industrial lime,

which hydrates, in favourable conditions, in the minute-to-hour scale. The slower hydration reaction of CFBC ash could be related to the phenomenon that ash solids are typically composed of an unreacted CaO_{free} core covered by a Ca-sulphate shell (Trikkel et al., 2000; Anthony & Granatstein, 2001). Thus, the lime hydration consists of two steps: slow water diffusion through the sulphate layer and fast lime hydration into portlandite. Similar processes probably take place during the carbonation of hydrated particles (4) when anhydrite and/or gypsum outer shell retard the CO_2 diffusion and slows the reaction kinetics (Kaljuvee et al., 1997).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (4)$$

Moreover, the CO_2 transport can be further inhibited by $CaCO_3$ formation in the outer perimeter of the hydrated portlandite particles, and the carbonation takes place during a much longer period of 58 days than in PF ash, where portlandite was carbonated already after 28 days (Kuusik et al., 2004).

The next important reaction of oil shale ash hydration involves anhydrite conversion to gypsum (5) and ettringite formation (6).

$$CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \qquad (5)$$
$$3Ca(OH)_2 + 2Al(OH)_3 + 3CaSO_4 + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O \quad (6)$$

Our results show that ettringite formation is not observed before all lime has been converted to portlandite, and portlandite to calcite transformation has started. Nevertheless, experimental results and kinetic modelling by Bernardo et al. (2004) suggest that ettringite formation occurs already after a few hours of hydration, and the rate of ettringite synthesis depends only on the availability of limiting reactant(s). They found that the CFBC ash hydration is regulated by Ca-sulphate (anhydrite) as the limiting reactant for the formation of ettringite. However, the calcareous oil shale ash is considerably richer in Ca-sulphate compared to silica-rich coal CFBC ash. Therefore, in the case of Estonian oil shale CFBC ash, anhydrite cannot be considered as a limiting factor for ettringite formation and the excess of anhydrite is evident from concurrent gypsum formation. Delayed ettringite formation can be explained by geochemical inhibitors of the crystallization. Mehta (1973) noted that the ettringite, formed in the presence of CaO_{free}, is colloidal and the longest dimension of diffuse particles does not exceed 1 μm, while typical well-crystalline ettringite is characterized by 5–10 μm long euhedral hexagonal prismatic fibre-like crystallites. Deng & Tang (1994) suggest that when an aluminium-bearing phase is hydrating in the presence of gypsum and lime, the lime depresses the solubility of the aluminium-bearing phase (aluminate, alumosilicate glass, clay minerals and K-feldspar), leading to high concentration gradients at these phase surfaces due to inhibited diffusion of $Al(OH)_4^-$ ions into the pore solution. Consequently, the interfaces of Al-phases are rapidly supersaturated with respect to ettringite, and

small crystals with limited growth precipitate from the solution at a high nucleation rate. Thus, we can suggest that ettringite is formed already during the initial phases of hydration, but only in colloidal (X-ray amorphous) form, and cannot be detected by XRD. At later stages, when all lime is hydrated to portlandite, the colloidal ettringite will transform into well-crystallized form. This could explain the "delayed" ettringite formation in oil shale ash observed in the current study and its absence in earlier reports (Kuusik et al., 2004).

Ettringite is an unstable mineral that starts to decompose under atmospheric conditions. As discussed above, the stability of ettringite is controlled by pH and the phase is stable at pH values >10.7. At lower pH values ettringite becomes unstable and dissolves incongruently to gypsum, (amorphous) Al-hydroxide and Ca-aluminate type phases; or in the presence of atmospheric CO_2 into Ca-sulphate, Al-gel and calcium carbonate polymorph – aragonite through vaterite as an intermediate phase (Grounds et al, 1988; Nishikawa et al., 1992; Myneni et al., 1998;). In our experiments, ettringite was decomposed into bassanite ($CaSO_4 \cdot 0.5H_2O$) and/or gypsum and calcite (7), which agrees with experiments by Nishikawa et al. (1992), with the exception that instead of aragonite/vaterite the stable calcite was identified.

$$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O + 3CO_2 \rightarrow 3CaCO_3 + 2Al(OH)_3 + 3CaSO_4 \cdot 0.5H_2O + 27.5H_2O \qquad (7)$$
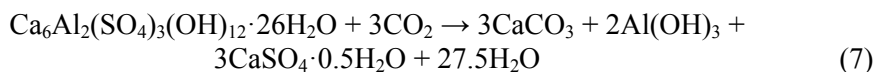
A large-scale deposition experiment with CFBC ash on the ash plateau of the Balti TPP shows a strong grain-size and compositional differentiation of ash in hydraulic deposition (PAPER IV). These differences cause variation in the geotechnical properties of ash. The coarse-grained ash fractions that deposit at the entrance of the channel yield lower compressive strength and tangent modulus, and therefore, the present hydraulic deposition technology, widely used for PF ash deposition, is not recommended for the deposition of CFBC ash.

Variation in the geotechnical characteristics of oil shale ash sediments is controlled by cementitious properties of ash fractions, which depend mainly on the composition and content of secondary Ca-phases – β-C2S and lime, and pozzolanic properties of the silicate glass phase (Piksarv, 1959; Dilaktorski et al., 1961; Galibina et al., 1965). The content of lime, β-C2S and amorphous glass phases in PF ash reaches the maximum of 70–80% in the fine fractions of electrostatic precipitator filters, but is also as high as 50–60% in the coarse-grained furnace ash fractions. As a result, the cementation properties of PF ash are good. However, the content of potential cementing phases in CFBC ash is considerably lower, since the ash is formed at significantly lower temperatures. First of all, the proportion of lime in the finest fractions separated in the electrostatic precipitators is at least twice lower in CFBC ash than in PF ash (PAPER II). Arro et al. (2005) have show that the electrostatic precipitator ash have the highest binding capacity and compressive strength, whereas the final compressive strength of hydrated PF ash mortars (15.4 N mm^{-2}) was three times higher than for the same fraction of CFBC ash.

The binding properties of lime are controlled by fast hydration of lime (slacking), which results in the formation of $Ca(OH)_2$ (portlandite) and its subsequent carbonation in the presence of atmospheric and/or dissolved CO_2. However, natural carbonation of ash sediments in waste deposits is rather slow due to limited availability of CO_2 in deeper parts of the ash deposit (PAPER V). Additional cementation of oil shale wastes is probably provided also by precipitation of secondary Ca(Al)-sulphate phases – ettringite, gypsum and hydrocalumite ($Ca_2Al(OH)_7 \cdot 3H_2O$) (PAPER I; PAPER III), but this type of cementation is rather weak and unstable, especially in leaching environments (percolating rainwater, etc.) where the pH of pore-water will drop below the values required for ettringite stability. Moreover, the amount of secondary Ca-silicate phases as well as of the amorphous glass phase in low-temperature CFBC ash is lower and the sediments have, thus, a lower pozzolanic potential.

Another problem emerging from the hydraulic deposition of CFBC ash is related to strong grain-size separation along the flow path. Grain size distribution of CFBC ash types varies in a wide range compared to that of PF ash, which is rather uniform (Kuusik et al., 2005). Moreover, the content of lime in different PF ash types is the highest (25–30%) in furnace ash, decreasing gradually along the ash collection path (Figure 2) all the way to the electrostatic precipitators (PAPER II). However, in CFBC ash, the content of lime in furnace ash is lower than in PF furnace ash (10–15%). The lime content reaches its maximum in the economizer–air-preheater zone and then decreases through the fields of electrostatic precipitators (PAPER II). At the entrance to the channel, the coarse-grained aggregates of irregular size are mainly composed of residual calcite and larger Ca-sulphate particles, which mostly originate from the CFBC furnace. The coarse structure and smaller proportion of lime in this sediment evidently do not provide necessary cementation. Pulverized firing ash, which has a more homogeneous grain size distribution, is free of such a separation problem. The higher proportion of lime of PF ash, especially in coarse-grained furnace ash, ensures also good cementation of the sediment irrespective of its position in the deposition system.

4.4. Composition and diagenesis of hydrated ash plateau sediments

Large ash waste plateaus of the Estonian TPP contain nearly 300 Mt of sediments occupying an area of about 20 km^2. At the current mining and power production level about 5–7 Mt of ash is added to the plateaus every year, whereas the reuse of the ash is very limited and only a small proportion (less than 5%) of total ash flow is used for construction materials (e.g. Portland cement, gas-concrete), in road construction (stabilization of roadbeds) and for agricultural purposes, e.g. liming of acid soils.

Oil shale is highly calcareous, and the ash remaining after combustion, derived from thermal decomposition of carbonate minerals, is rich in lime and

anhydrite (PAPER II). During hydration of ash already in the transportation system and later under open atmospheric storage in plateaus the dissolution of secondary Ca-phases (e.g. portlandite, Ca–Al-sulphate – ettringite) causes high alkalinity (pH 12–13) of the water draining off the plateaus. The highly alkaline leachates from the ash plateau deposits pose an environmental risk, and the ash plateaus are considered as major pollution sources (Savitskaja, 1997).

The alkalinity potential of ash waste depends directly on the mineral composition and diagenetic evolution of the sediment. The average mineral composition of ash deposited on the ash plateaus is dominated by lime (17%), anhydrite (10%) and β-C2S (11%). The first two mineral phases are unstable under hydrous conditions and are rapidly hydrated/transformed into metastable hydrous phases. The experimental hydration of oil shale PF and CFBC ash (Kuusik et al., 2004; PAPER III) suggests that the lime to portlandite conversion is fast, and almost complete lime slacking occurs during the first 24 hours of reaction. The next stage of oil shale ash hydration is governed by anhydrite (anhydrous Ca-sulphate) reactions towards gypsum and ettringite (PAPER III).

The formation of hydrocalumite as the next secondary phase in the PF ash hydration process suggests that ettringite formation in oil shale ash is limited by the availability of dissolved sulphate, while the excess of aluminium is precipitated as Ca-aluminate(hydrate) (hydrocalumite) type phases. However, Liira et al. (PAPER III) noted that in CFBC ash ettringite formation is accompanied by precipitation of excess gypsum, which implies that aluminium, not sulphate, is a limiting component in this ash.

In hydration experiments (Kuusik et al., 2004; PAPER III) subsequent diagenetic transformation of hydrated ash is governed by carbonation of the metastable portlandite by binding atmospheric CO_2, which is completed under ambient conditions (allowing free transport of CO_2) in a few weeks and months. In plateaus, however, significant (but not complete) carbonation of portlandite is achieved only in the uppermost 0.5–1 m thick layer of the deposit. The content of calcite decreases over (through) an about 5 m thick depth interval, whereas portlandite is well preserved in deeper parts of the ash plateau sequence (PAPER V). This suggests slow carbonation of plateau sediments by controlled CO_2 diffusion, which is further retarded in the upper layers of the ash deposits due to effective precipitation of calcite and other secondary minerals, which will progressively block out the pore space.

Slow carbonation of ash sediments is important in retaining the stability of other primary hydration phases, especially ettringite. Portlandite dissolution equilibrium controls the solution pH at pH ~12.3, which is well above the ettringite stability limit (pH 10.7), and in deeper parts of the ash plateau ettringite is in a stable phase. However, calcite equilibrium (pH ~8.2) is attained by carbonation of portlandite in the system and ettringite becomes unstable. This process is evident only in the uppermost layer of plateau sediments, where the proportion of ettringite has somewhat decreased, but in the presence of some amounts of portlandite the pH is still at the ettringite stability level (pH ~12).

Diagenetic transformation of the secondary Ca-silicate phases, formed in the combustion processes, is subdued, although β-C2S can react with atmospheric CO_2, forming additional calcite and quartz.

The mineralogical data suggest the dissolution of amorphous glass phases and precipitation of secondary smectite type clay phases. High activity of dissolved Si and specifically high K (>500 mg L^{-1}) (Kõiv et al., 2010) in the water in contact with ash would hint on the precipitation of secondary mixed-layer clays, zeolites and/or authigenic K-feldspar phases, similar to hydration of volcanic glasses in evaporitic alkaline hypersaline or diagenetic environments. However, secondary silicates other than smectite type clay were not identified in the plateau sediments.

High alkalinity (pH 12–13) of the water draining off the ash sediment plateaus is controlled by the proportions of portlandite and ettringite, which are the main secondary Ca-hydrate phases in plateau sediments. Our results show that stabilization of plateau sediments by carbonation and precipitation of stable calcite has affected only a limited volume of surface sediments, which means that the sediment heaps retain a high alkalinity potential for a long time (PAPER V). The alkalinity (potential) or buffering capacity of ash sediments can be estimated as a function of the concentrations of alkaline elements and cations of strong bases (Ca, Mg and Na, K, respectively) (Hjelmar, 1990; Kim, 2006). The average proportion of non-silicate Ca in ash plateau sediments is 25%, and the corresponding average estimated alkalinity of ash sediments is thus 1195 meq_{NaOH} g^{-1} (PAPER V).

Under open conditions the ash alkalinity is neutralized mainly by slightly acidic (pH 5.65) natural precipitation. The precipitation water in equilibrium with atmospheric CO_2 contains 9.3×10^{-6} mol L^{-1} of carbonic acid, which suggests that about 7×10^5 L of rain water is required for full neutralization (pH 7) of 1 kg of ash sediments. As the mean annual precipitation in Estonia is about 760 mm yr^{-1}, the neutralization of one cubic metre of ash sediments requires a percolating rainwater volume equivalent to the precipitation in about 400 thousand years. Although this is a rough, most probably over-dimensioned estimate, it is evident that hydrated oil shale ash sediments maintain high alkalinity and alkaline pH for a considerably long time, posing a potential environmental threat for the coming centuries.

6. CONCLUSIONS

1) Oil shale semi-coke is a complex mixture of residual organics, transformed mineral matter, macroscopically unaltered oil shale and pieces of carbonate rock. The composition of fresh semi-coke reflects the changes in mineral matter in the retorting process. During the main phase of retorting at 400–520 °C the changes in oil shale mineral matter are negligible, still, dehydration and partial transformation of clay minerals and decomposition of sulphur compounds (pyrite, marcasite) take place. Most significant changes in the composition of retorted shale occur during the final stage of the retorting process, when higher temperatures (900–1000 °C) are applied to remove the residual carbon compounds. During this phase slag-like materials form, consisting of the amorphous glass phase and Ca-silicate phases.

2) Hydrated semi-coke sediments are characterized by a high content of secondary Ca–Al-sulphate mineral ettringite (up to 20%), which causes cementation of loose semi-coke particles in waste deposits. However, ettringite is a stable phase only at elevated pH levels and is slowly dissolved by percolating unsaturated precipitation water.

3) The composition and particle micromorphology of pulverized firing (PF) and circulating fluidized bed boiler combustion (CFBC) ash are principally controlled by firing temperature differences in the respective combustion technologies, and by grain size differences of raw oil shale fuel. Pulverized firing ash are dominated by lime (CaO_{free}), whose proportion decreases from the furnace to the last fields of electrostatic precipitators, but the composition and distribution of phases in ash fractions from CFBC boilers is more complex. Comparison of the phase composition of ash from the same type of boilers in the Eesti and Balti TPPs shows remarkable differences in Ca-silicate phases, which can be interpreted as caused by variations in oil shale fuel used at these power plants rather than by combustion technology.

4) A laboratory scale hydration experiment with CFBC ash suggests rapid initial hydration reactions during the first 72 h: lime to portlandite reaction and anhydrite and periclase dissolution, followed by the formation of ettringite after 144 h in open atmospheric conditions, and finally slow carbonation accompanied by decomposition of ettringite into calcite and the Ca-sulphate hemihydrates phase. The hydration of oil shale CFBC ash is particularly characterized by a high content of ettringite.

5) A large-scale deposition experiment with CFBC ash on the ash plateau shows a strong grain-size and compositional differentiation of CFBC ash in hydraulic deposition. Compared to PF ash, CFBC ash has lower cementation properties due to a characteristic phase composition resulting from considerably lower combustion temperature and enhanced phase separation. In

hydraulic deposition the physical separation of CFBC ash particles causes further partition of the cementation phases, which results in weaker geo-technical properties of CFBC ash sediments compared to PF ash sediment deposits. The hydraulic transport of CFBC ash to the ash plateaus is not suitable for building peripheral dams in these ash deposits.

6) The carbonation of hydrated ash sediments in open plateau deposits is due to slow/limited CO_2 transport in only the uppermost a few metres thick layer. Slow carbonation allows preservation of primary hydration phases, such as ettringite and portlandite in deeper parts of the deposit. Ettringite and port-landite dissolution maintains the pH 12–13 of the infiltrating precipitation water, which needs treatment before discharge into water bodies. However, the alkalinity potential estimated from the composition of ash shows that the full neutralization of ash sediments by precipitation water would require hundreds of thousands of years, thus making these ash plateaus an environ-mental problem for many coming generations.

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SUMMARY IN ESTONIAN

PÕLEVKIVITÖÖSTUSE TAHKETE
JÄÄTMETE KOOSTIS JA DIAGENEES

Käesolev doktoritöö uurib Eesti põlevkivitööstuse tahkete jäätmete, poolkoksi ja põlevkivituha koostist ning selle muutlikkust pikaajalisel ladustamisel.

Tänane Eesti energeetikasektor tugineb enam kui 90% osas põlevkivienergeetikal, mis kasutab karjääriviisiliselt ja maa-alustes kaevandustes kaevandatavat Ordoviitsiumi kerogeeni sisaldavat savikivimit – põlevkivi ehk kukersiiti. Põlevkivi on suhteliselt madala kütteväärtusega põlevmaavara, mille põletamisel ja/või keemilisel töötlemisel tekib suures koguses jääkprodukte – tuhka ja poolkoksi. Suurtes Eesti põlevkivil töötavates soojuselektrijaamades – Balti ja Eesti soojuselektrijaamas (ekspluatatsiooni vastavalt 1959 ja 1969) – on tuhaplatoodele ladestatud juba ligemale 300 miljonit tonni põletusjäätmeid. Sellele lisandub umbes 100 miljonit tonni põlevkivi utmisjääke – poolkoksi. Praeguse elektrienergia ja põlevkiviõli tootmise tempo juures lisandub umbes 5–7 miljonit tonni tuhka ja ligikaudu 1 miljon tonni poolkoksi aastas.

Põlevkivi põletamisel ja keemiatööstuses tekkivate jäätmete taaskasutamine on olnud väga piiratud ja kindlasti ebapiisav. Siiani on leidnud sisulist rakendust vaid elektrijaamades tekkiva tuha peeneteralised fraktsioonid (lendtuhk), mille kogumassist on varasematel aastatel kasutatud kuni 5%. Seetõttu on valdav enamus tuhast ja poolkoksist ladustatud elektrijaamade vahetus naabruses paiknevatesse jäätmehoidlatesse.

Põlevkivituhaplatood ja poolkoksiladestud kujutavad endast keskkonna püsireostusallikaid ning neid käsitletakse Eesti kõige ohtlikumate keskkonnaprobleemidena. Tuha ja poolkoksi ladestute peamiseks keskkonnaprobleemiks on tuha ning poolkoksi hüdratiseerumisel tekkiva nõrgvee kõrge leeliselisus ja platoode geotehniline stabiilsus. Poolkoksi ladestustes lisandub nendele probleemidele orgaaniliste ühendite (peamiselt fenoolide) reostusoht. Tuhaplatoode nõrgvee pH ulatub kuni 12–13-ni, kuid keskkonnanormidele vastavalt peab loodusesse juhitavate vete pH olema alla 9. Leeliselise nõrgvee moodustumine ja lasundite stabiilsus on otseselt seotud reaktsioonidega, mida kontrollivad jäätmete keemiline ning mineraalne koostis, mille selgitamine oli käesoleva doktoritöö uurimisprobleemi üldeesmärgiks.

Käesoleva doktoritöö põhitulemused näitavad, et:
1) Põlevkivi poolkoks on mitmekomponendiline segu utmise jääkproduktidest – orgaanilisest ainesest, muundunud põlevkivi mineraalosast ning muutumatuna või vähesel määral muutunud põlevkivist (sh karbonaatne osa). Utmise põhifaasis, orgaanilise ainese termokatalüütilisel lagunemisel temperatuuridel 400–520 °C ei toimu olulisi muutusi mineraalsetes komponentides, küll aga algab saviminemeraalide lagunemine ning väävli ja raua järk-järguline vabanemine püriidi/markasiidi termaalse dissotsiatsiooni tulemusena. Tähelepanuväärsemad muutused toimuvad poolkoksis utmise lõppfaasis, kui

temperatuur tõstetakse orgaanilise ainese väljapõletamise eesmärgil lühikeseks ajaks 900–1000 °C-ni. Selles faasis toimub poolkoksi šlakistumine, mille põhilisteks saadusteks on amorfne klaas ja sekundaarsed Ca-silikaatsed faasid. Poolkoksi hüdratiseerumisel jäätmeladestutes toimub selle mineraalses koostises rida olulisi muutusi, millest iseloomulikumaks on Ca–Al-sulfaadi – ettringiidi moodustumine. Ettringiit täidab efektiivselt poolkoksi sette pooriruumi sidudes setteosakesi ühtseks tsementeerunud tervikuks, tugevdades seeläbi jäätmelasundi geotehnilist püsivust. Siiski on ettringiit stabiilne vaid kõrgetel pH väärtustel ning see mineraal laguneb aeglaselt ladestute pinnakihis sademete leostuval toimel.

2) Elektritootmises kasutatavate tolmpõletuskatelde (PF) ja keevkihtkatelde (CFBC) tuha koostist, osakeste suurust ja kuju mõjutab enim põlemistemperatuur ja põletatava kütuse peensuse aste. Kõrgetemperatuurilises PF tuhas esineb domineeriva faasina kustutamata lubi, mille osakaal langeb tuhaärastussüsteemis katlast elektrifiltrite suunas. Samas suureneb peenemates tuhafraktsioonides sekundaarsete Ca-silikaatide osakaal. Keevkihtkatelde tuha koostis ja erinevate faaside jaotumine tuhaärastussüsteemis on oluliselt keerulisema käitumisega ning selle tuha põhikomponentide sisaldused ei järgi PF tuhafraktsioonidele iseloomulikke lineaarseid trende. Näiteks toimub keevkihtkatelde tuhas spetsiifiline Ca-sulfaadi koondumine INTREX™ soojusvaheti tuhas. Sõltumata põletusrežiimist avastati süstemaatiline erinevus Balti ja Eesti soojuselektrijaama sama tüüpi katelde põlevkivituha koostises, mida iseloomustab Ca-silikaatide kvalitatiivse koostise varieerumine. Tõenäoliselt põhjustab neid erinevusi elektrijaamades kasutatava kütuse koostise varieeruvus, mitte aga põletustingimused.

3) Viimase kuue aasta jooksul Eesti elektrijaamades tööle rakendatud efektiivsemate ja keskkonnasäästlikumate keevkihtkatelde tuha hüdratiseerumise käik ja tsementeerunud tuhasette geotehnilised omadused erinevad oluliselt tolmpõletuse tuhast/tuhasettest. Keevkihtkatelde tuhasette tüüpiliseks koostisosaks on sarnaselt poolkoksiga Ca–Al-sulfaat – ettringiit, mille kristalliseerumine loob esialgselt piisavalt tsementeerunud karkassi, kuid mis on atmosfääri tingimustes ebastabiilne lagunedes kaltsiidiks ja Ca-poolhüdraat faasideks.

4) Keevkihtkatelde tuhaga läbi viidud suuremõõtmelise hüdraulilise ladestamiskatse käigus ilmnes tuhaosakeste tugev fraktsioneerumine ning sellest tulenevalt sette keemilise ja mineraalse koostise ja füüsiliste omaduste varieerumine. Võrreldes PF tuhaga on CFBC tuhal sõltuvalt madalamast põletustemperatuurist väiksem potentsiaalselt tsementeeruvate faaside sisaldus, mistõttu on CFBC tuhasete halvemate geotehniliste omadustega. Nõrgemat tsementeeruvust võimendab veelgi tuhaosakeste separeerumine hüdraulilisel ladestamisel. Seepärast ei ole CFBC tuha ladestamisel võimalik kasutada endist märgladestustehnoloogiat.

5) Hüdratiseerunud tuhasette karboniseerumine on CO_2 aeglase või piiratud juurdepääsu tõttu limiteeritud vaid tuhasette ülemise mõne meetri paksuse kihiga. Samas võimaldab aeglane karboniseerumine säilitada tuhalademe

sügavamas osas primaarseid hüdratiseerumisprodukte nagu ettringiit ja port-landiit, millel on oluline roll setteladestu geotehnilise stabiilsuse tagamisel. Paraku on selle protsessi ebasoovitavaks tulemiks tuhalademetesse infilt-reeruva vee äärmiselt kõrge leeliselisus (pH 12–13). Arvutuslikult, eeldades leeliselisuse neutraliseerumist ainult sademetevee mõjul, kuluks tuhasette leeliselisuse potentsiaali täielikuks neutraliseerumiseks sadade tuhandete aastate Eesti keskmine sademetehulk, mis muudab tuhajäätmed ökoloogi-liseks probleemiks paljude tulevaste põlvkondade jaoks.

ACKNOWLEDGEMENTS

Above all I wish to express my greatest gratitude to my supervisor, prof. Kalle Kirsimäe, who has helped me through all these years, not only in doctoral studies but from the beginning of my studies at the university.

Most certainly I would like to thank my colleagues and friends from the days in our old room No. 244, without their sometimes more sometimes less fruitful and philosophical discussions these studies would have been much less fun. Many thanks go to our team of project No.EU23687.

PUBLICATIONS

CURRICULUM VITAE

Riho Mõtlep

Date of birth: 10.02.1980
Address: Department of Geology, Ravila 14a, 50411, Tartu, Estonia
Contact: Phone, +372 737 6689
                   Fax, +372 737 5836
E-mail: riho.motlep@ut.ee

Education

2006–…   University of Tartu, PhD studies, environmental technology.
2004–2006   University of Tartu, MSc environmental technology.
1998–2004   University of Tartu, BSc geology.

Professional employment

2006–...   Specialist of technology at University of Tartu,
              Department of Geology.

Research activity

Field of research:
– Mineralogy and geochemistry; the composition and diagenesis of oil shale industry solid wastes.

Publications

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ELULOOKIRJELDUS

Riho Mõtlep

Sünniaeg: 10.02.1980
Aadress: Geoloogia osakond, Ravila 14a, 50411, Tartu, Eesti
Kontakt: Tel, +372 737 6689
              Fax, +372 737 5836
E-mail: riho.motlep@ut.ee

Haridus

2006–…   Tartu Ülikool, keskkonnatehnoloogia doktorant.
2004–2006   Tartu Ülikool, MSc keskkonnatehnoloogias.
1998–2004   Tartu Ülikool, BSc geoloogias.

Teenistuskäik

2006–...   Tartu Ülikool, Geoloogia osakond; tehnoloogia spetsialist.

Teadustegevus

Teadustöö põhisuunad:
– Mineraloogia ja geokeemia; põlevkivitööstuse tahkete jäätmete koostis ja muutumine.

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