

ANNETTE SEDMAN

Strength and self-cementing properties
of oil shale retorting wastes



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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 **Sedman, A.**, Talviste, P., Mõtlep, R., Jõelett, A., Kirsimäe, K., 2012. Geotechnical characterization of Estonian oil shale semi-coke deposits with prime emphasis on their shear strength. *Engineering Geology*, 131–132, 37–44.
- II Talviste, P., **Sedman, A.**, Mõtlep, R., Kirsimäe, K., 2013. Self-cementing properties of oil shale solid heat carrier retorting residue. *Waste Management and Research*, 31 (in press), doi: 10.1177/0734242X13482033.
- III **Sedman, A.**, Talviste, P., Kirsimäe, K., 2012. The study of hydration and carbonation reactions and corresponding changes in the physical properties of co-deposited oil shale ash and semicoke wastes in a small-scale field experiment. *Oil Shale*, 29(3), 279–294.

Author's contribution

Paper I: The author was responsible for planning original research, laboratory experiment and analysis, and interpretation of analytical data (about 50%), and primarily responsible for writing of the manuscript.

Paper II: The author was responsible for planning and running of experiments, collection of geotechnical data, interpretation and synthesis of geotechnical, chemical and mineralogical analysis, and writing of the manuscript (about 50%).

Paper III: The author was responsible for experiment planning and fieldwork, obtaining and interpretation of geotechnical data, and primarily responsible for writing of the manuscript.

I. INTRODUCTION

The growing demand for energy forces utilization of lower quality fossil fuels, such as oil shales. Oil shales are a diverse group of fine-grained sedimentary rocks containing significant amounts of bituminous organic matter (Craig et al., 2001), which can be pyrolysed to extract shale oil or burned in thermal power plants (TPP-s) to produce electricity and heat. Although oil shale is found all over the world, its industrial usage is limited to few countries including Brazil, China, Estonia, and Israel (World Energy Council, 2010). Effective and sustainable usage of oil shale is still problematic due to technological and environmental issues. Nevertheless, oil shale's perspectives were seen more positively in last decade (Brendow, 2003), and several oil shale reserves have been re-evaluated in the light of declining petroleum resources and increasing prices. These include, for example the Green River Formation in the USA (Johnson et al., 2004; Dyni, 2006; Andrews, 2008), Huadian deposits in China (Jiang et al., 2007; Wang et al., 2012), Jordan's oil shale reserves (Hrayshat, 2008), and Queensland deposits in Australia (Schmidt, 2003).

Estonia has practiced industrial scale usage of oil shale for more than 90 years due to relatively simple mining conditions and a high organic matter content of Estonian kukersite oil shale. Kukersite oil shale is found in North-East Estonia and North-West Russia, but only the Estonia deposit is currently actively used (Bauert and Kattai, 1997). Kukersite oil shale is composed of organic, carbonate and terrigenous material in various proportions. The content of organic matter ranges between 10–60% and is mostly composed of kerogen, but also contains a few per cent of bitumen (Koel, 1999). The organic part is mainly derived from residues of the colonial microorganism *Gloeocapsomorpha prisca* (Lille, 2003). The calorific value depends on the content of organic matter, which gradually decreases toward peripheral parts of the deposits, and in commercial oil shale beds the calorific value is on average 9–10 MJ/kg (Bauert and Kattai, 1997). The content of carbonates (calcite, dolomite) is 20–70%, and the terrigenous part (quartz, K-feldspar and clay minerals) comprises 15–60% of the rock (Bauert and Kattai, 1997).

The annual oil shale mining output in Estonia in the past five years has been at the level of 12–15 Mt (Statistics Estonia, 2013a). Estonia is exceptional by its oil shale usage. Usually oil shale is utilized as shale oil, but in Estonia, approximately 80% of mined oil shale is burned in TPP-s for electricity and heat generation. This is done using pulverized fuel (PF) or circulating fluidized bed (CFBC) combustion, where the temperatures reach about 1300 °C and 700–850 °C, accordingly. Most of the remaining mined oil shale is retorted to produce shale oil and gas (Ots, 2006). During the retorting process, oil shale is heated in the absence of oxygen to the temperature at which its organic part decomposes into gas and condensable oil, while the inorganic part remains in the form of retorting residue (Koel, 1999). Gas generator (e.g. Kiviter technology) and solid heat carrier (SHC) technology (e.g. Galoter, Petroter and

Enefit technologies) are used to produce shale oil in Estonia. Until recently, the gas generator technology dominated, but now shale oil producers are shifting their focus on new powerful SHC retorting facilities. However, both technologies have advantages and disadvantages: the gas generator technology cannot accept oil shale particles smaller than 25 mm, whereas the SHC technology requires fines smaller than 25 mm. Thus, they complement each other for the full utilization of the oil shale resource (Koel, 1999).

An unavoidable problem accompanying the usage of oil shale is the formation of huge amounts of environmentally hazardous solid wastes due to oil shale's high content of inorganic material. In the Estonian oil shale industry, nearly half of the oil shale's dry mass leaves the processing as solid wastes – oil shale ash from TPP-s and retorting residues from shale oil production. Most of the waste comes from the power industry – according to Statistics Estonia (2013b), in 2007–2011, 5–7.5 Mt of ash was formed annually. At the same time, the annual output of retorting waste from the shale oil industry was about 1–1.5 Mt (Statistics Estonia, 2013b), but the proportion of retorting wastes shows an increasing trend.

Oil shale ash is a light-colored mineral material that is composed of lime, calcite, anhydrate, different secondary Ca-silicate phases and a residual non-carbonate fraction in varying proportions (Bityukova, 2010). Although ash has been partially reused in the past as a constituent in cement, in road construction and for agricultural purposes (Pets et al., 1984; Hanni, 1996), and new applications are studied (Vohla et al., 2005; Kaasik et al., 2008; Liira et al., 2009; Kõiv et al., 2010, 2012), the actual reuse is still marginal due to technological and economic problems. As a result, most of the ash is landfilled: ash from TPP-s is hydraulically transported in slurry with a water-to-ash ratio of 20:1 to sedimentation ponds, where it solidifies due to good self-cementing properties (Bityukova et al., 2010; Mõtlep et al., 2010), and up to 50 m high stabilized ash plateaus with steep slopes have formed as a result. The plateaus occupy an area of about 20 km² and accommodate more than 300 Mt of ash (Mõtlep et al., 2010).

Although the total amount of retorting waste is smaller compared to ash, it is still considered more problematic, because unlike combustion ash, retorting wastes contain organic residues that pose a potential environmental threat. Shale oil retorting produces two different types of waste depending on the technology used: blackish semi-coke from the gas generator process and dark grey retorting ash (hereinafter black ash) from the SHC process. Semi-coke is a poorly sorted black granular material with an organics content of up to 10%. Its mineral part contains predominantly minerals that are characteristic to raw oil shale, but also smaller amounts of phases that have formed due to partial thermal decomposition and reactions taking place in the final stage of the retorting process (Mõtlep et al., 2007). Although some potential re-use applications have been investigated (for example, as a sorbent, a source for activated carbon or as an additional fuel in cement industry) (Trikkel et al., 2004, 2008; Külaots et al.,

2010), most of the semi-coke is disposed of in special semi-coke landfills near the towns Kohtla-Järve and Kiviõli. More than 100 Mt of semi-coke has been deposited since the beginning of oil production in 1921 (Kattai, 2003). Compared to ash, semi-coke exhibits weaker cementitious properties (Mõtlep et al., 2007), causing technological problems during deposition. Black ash, the other retorting residue, is more similar to combustion ash. It contains only a few per cent of organics, because during the SHC process, the initial residue is heated up in the presence of oxygen and directed back to the retort chamber. So far, black ash has been deposited together with oil shale ash and thus little is known about its specific properties.

The structural, chemical and mineralogical properties of oil shale ash have been thoroughly studied recently (e.g. Paat, 2002; Kuusik et al., 2004; Kuusik et al., 2005; Liira et al., 2009; Bityukova et al., 2010; Mõtlep et al., 2010; Pihu et al., 2012). However, less is known about the retorting wastes, especially their geotechnical and self-cementing properties, although these properties determine the design and mechanical behavior of the landfills. The area for the landfills at an economically reasonable distance from shale oil plants is a limited resource, and therefore, the dumps should be as high as possible to accommodate large amounts of waste. Mechanical stability of the deposits is extremely important for avoiding failure of the waste piles, potential leaching of hazardous components and contamination of the surroundings. These aspects are highly influenced by the geotechnical and physical properties of waste materials that, among other factors, depend on mineral alteration and the development of cementation in the disposed material. Thus, the geotechnical/physical properties and mineral composition should be analyzed together to explain the long-term behavior and stability of the waste deposits.

The current thesis focuses on retorting wastes, aiming to improve the management of semi-coke and black ash. To our best knowledge, there are no comprehensive data about Estonian SHC black ash, but the employment of new powerful SHC retorts has raised the need for a well-planned disposal technique. Also another potential disposal method – co-disposal of semi-coke and oil shale ash – has been proposed.

The objectives of this dissertation are to:

- examine the strength properties of semi-coke waste deposits and to study the development of cementation, which helps to evaluate the long-term stability of huge semi-coke dumps and plan new disposal activities;
- study the self-cementing properties and mineral transformation of black ash by simulating different disposal methods, in order to evaluate the suitability of potential landfilling methods in terms of mechanical stability;
- study the potential co-disposal of oil shale ash and semi-coke in a small-scale field experiment.

2. MATERIAL AND METHODS

Each waste material is different, and thus, a universal testing program cannot be used. The strength properties of granular/loose materials are usually estimated using shear strength, while the cemented materials are better described using compressive strength. The semi-coke type of retorting waste tends to exhibit weaker cementation and its properties were assessed using shear strength. Black ash, on the other hand, shows good self-cementing properties, thus compressive strength testing was used. In the co-disposal experiment of semi-coke and oil shale ash, hydraulic conductivity and dry density of the mixtures were measured, because it was the best way to describe the expansion and cracking mechanism occurring in the mixtures.

As the values of geotechnical properties alone do not carry information about the nature of cementing bonds and the long term stability of measured values, also the mineral transformation was studied, focusing on the secondary cementing phases that contribute to strength development.

2.1. Semi-coke

A total of more than 200 samples from three structural types of semi-coke were collected from 1–1.5 m deep excavations or surface layers of old and new parts of semi-coke landfills near Kohtla-Järve and Kiviõli. Undisturbed and remolded samples were collected in order to study the properties of cemented and non-cemented material.

Strength properties were assessed by drained direct shear strength tests (ETC5-F2.97) at a vertical normal stress range of 10–800 kPa on 178 specimens at the Geotechnical Laboratory of the Estonian Environmental Research Centre. According to the Mohr–Coulomb theory, shear strength is a function of soil properties and applied normal stress: $s = \sigma' \tan \varphi' + c'$, where s is shear stress at failure, σ' the effective normal stress, φ' the effective friction angle and c' the effective cohesion (Mitchell and Soga, 2005). Whereas effective normal stress is subject to change, shear strength is usually characterized by the friction angle and cohesion, which can be considered constant within the range of stresses normally encountered in the field (Coduto, 1999).

Shear strength tests were performed on undisturbed (monolithic) and remolded samples. Remolded samples were tested at their natural water content (unsaturated state) and at a nearly saturated state, because soil exhibits the lowest strength at saturated conditions, which may occasionally prevail in the deposits. However, it appeared that fully saturated conditions were not achieved, because entrapped air remained in the pores of semi-coke. Thus, the samples are referred to as quasi-saturated *sensu* Faybishenko (1995) and Sakaguchi et al. (2005). The well graded semi-coke samples were saturated under vacuum conditions for 15 days to obtain an approximate estimation of the

saturation process in time. Also hydrophobicity was determined on monolithic samples using the water drop penetration time (WDPT) test (Letey, 1969).

In addition, other geotechnical parameters, including grain size distribution (ETC5-C4.97), dry density (ETC5-C2.97), water content (ETC5-C1.97) and specific gravity of solids (ETC5-C3.97) were measured using standard procedures at the Geotechnical Laboratory of the Estonian Environmental Research Centre.

2.2. Black ash

The analyzed black ash came from the Petroter SHC retort, Viru Keemia Grupp AS (Kohtla-Järve, Estonia). Fresh dry black ash was stored in airtight containers prior to the analysis. Firstly, the composition and physical properties of fresh unhydrated ash were studied. Secondly, monolithic samples were prepared for examining the self-cementing properties and composition of the hydrated material. The samples were prepared by mixing dry black ash with water at the saturated conditions. The samples were placed into cylindrical PVC tubes (10 cm in diameter and 12 cm high). Cementation of black ash was studied, imitating alternative disposal methods currently used in the Estonian oil shale industry: (1) dry dumping of moist material; (2) hydraulic disposal without grain size separation; (3) hydraulic disposal with grain size separation. The samples were stored in the laboratory either in water tanks under permanent saturation or in ambient air after the initial mixing with water. A detailed description of the samples and storing conditions is given in Table 1.

For imitating hydraulic disposal with grain size separation, the material was sieved into two fractions – fine ($<125\ \mu\text{m}$) and coarse ($>125\ \mu\text{m}$). If the ash-water mixture spreads in ponds with a flat and sub-horizontal ($<0.05\ \text{m}\cdot\text{m}^{-1}$) bottom as a thin ($<20\ \text{cm}$) flow sheet in a $>20\ \text{m}$ wide channel, the flow speed is assumed to be $1\ \text{m}\cdot\text{s}^{-1}$ at the entrance point of the ash transportation pipe line and $<0.01\ \text{m}\cdot\text{s}^{-1}$ in the distal parts of the pond (Pihu et al., 2012). Using the Shields-Rouse equation (Chien and Wan, 1999), we estimated that in the proximal part of the basin where water flow decreases to $<0.05\ \text{m}\cdot\text{s}^{-1}$, particles $>125\ \mu\text{m}$ in size are deposited. Finer particles ($<125\ \mu\text{m}$) are kept in motion until the flow rate drops to $0.01\ \text{m}\cdot\text{s}^{-1}$, which characterizes the distal part of the sedimentation basin.

The self-cementing properties of black ash were evaluated by uniaxial compressive strength tests under continuous loading ($20\ \text{kPa}\cdot\text{s}^{-1}$) until the specimen broke. Compressive strength was measured in three (in a few cases two) replicas after 5, 15, 30 and 90 days. Altogether 55 compressive strength tests were conducted in the Laboratory of Construction Materials in Estonian University of Life Sciences. Other physical properties, including density (ρ) (ETC5-C2.97) and water content (w) (ETC5-C1.97) were measured in each monolithic specimen used for compressive strength tests. Dry density (ρ_d) was

calculated using the equation $\rho_d = \rho \cdot (1 + w)^{-1}$ (e.g. Coduto, 1999). The grain size distribution (ETC5-C4.97) and the specific gravity of solids (G_s) (ETC5-3.97) of fresh material were also determined.

Table 1. Description of the samples, storing conditions and the imitated disposal methods (after Paper II – Talviste et al., 2013).

Sample	Description of the sample	Storing conditions	Disposal method
ASH _a	Unsorted ash mixed with water, 2:1ratio	In ambient air	Dry dumping of moist material
ASH _w	Unsorted ash mixed with water, 2:1ratio	In water tank	Hydraulic disposal without grain size separation
<125 _a	Fraction of <125 μm mixed with water, 1.5:1 ratio	5 days in water tank, afterwards in ambient air	Hydraulic disposal with grain size separation with drainage of the pond
<125 _w	Fraction of <125 μm mixed with water, 1.5:1 ratio	In water tank	Hydraulic disposal with grain size separation; under water
>125 _a	Fraction of >125 μm mixed with water, 2.5:1 ratio	5 days in water tank, afterwards in ambient air	Hydraulic disposal with grain size separation with drainage of the pond
>125 _w	Fraction of >125 μm mixed with water, 2.5:1 ratio	In water tank	Hydraulic disposal with grain size separation; under water

2.3. Co-deposition experiment

A small-scale field experiment was conducted in the semi-coke landfill operated by Viru Keemia Grupp AS (Kohtla-Järve, Estonia). The material was also provided by Viru Keemia Grupp AS. Fresh moist semi-coke from the Kiviter retort and fresh dry ash from the PF generator at Põhja TPP were used. Ash and semi-coke were mechanically mixed, placed into wooden boxes ($2 \times 3 \times 0.6$ m) and compacted using a portable vibratory plate compactor. Five different mixtures with ash and semi-coke ratios (by volume) of 1:4, 1:3, 1:2, 1:1 and 2:1 were prepared and left under field conditions for about a four month period.

During the experiment, hydraulic conductivity (k), dry density (ρ_d), water content (w) and mineral composition of the mixtures were determined after 1, 2, and 4 weeks, and 2 and 4 months. Weather conditions were recorded by the Jõhvi automatic weather station (Estonian Institute of Meteorology and Hydrology), which is situated about 13 km south-east from the testing site. Hydraulic conductivity was measured *in situ* at a depth of 0.2–0.3 m from the

surface in pre-drilled holes with a diameter of 30 mm, using a falling-head permeability testing device GeoN Permeameter Pi301. Undisturbed samples from each mixture were collected from the same depth for dry density and water content measurements, performed at the Geotechnical Laboratory of Estonian Environmental Research Centre. An additional hydraulic conductivity measurement was undertaken 11–12 months after the initial measurements, with the mixtures having been exposed to weather conditions. Hydraulic conductivity was measured below the uppermost weathered layer at a depth of 0.4–0.6 m.

2.4. Analytical methods

The mineral composition of black ash and semi-coke-ash mixtures was examined using X-ray diffractometry (XRD) on a Bruker D8 Advance diffractometer at the Department of Geology, University of Tartu. The quantitative mineral composition of the samples was modeled by the Siroquant 3.0 Rietveld code (Taylor et al., 1991). The chemical composition of black ash was studied using X-ray fluorescence analysis on a Rigaku Primus II spectrometer. Scanning electron microscopy (SEM) imaging of semi-coke samples was undertaken on a Zeiss EVO MA15 SEM equipped with an Oxford Aztec energy dispersive X-ray analytical system to study the micromorphology and inner structure of the material.

3. RESULTS AND DISCUSSION

In the first chapter (3.1.), the strength properties of semi-coke deposits are discussed. The second chapter (3.2.) addresses the self-cementing properties of black ash; the suitability of different disposal methods is assessed as well. The third chapter (3.3.) covers the co-disposal of semi-coke and oil shale ash experiment.

3.1. Semi-coke deposits

The shear strength development and related properties of semi-coke deposits are discussed in Paper I – Sedman et al., 2012a.

The structure of semi-coke deposits is highly heterogeneous. Fresh semi-coke is a loose material, but after disposal, unstable phases start to change and cementing bonds form between particles, leading to the formation of more or less monolithic zones. However, this cementation is not evenly distributed, giving the deposits an irregular layered nature with stronger and softer zones. In addition, shale-like, conglomerate-like and well graded structural types of semi-coke can be distinguished in the deposits, depending on the used disposal methods. Until the early 2000s, semi-coke was carried to the top of the waste heaps by wagons and washed down with water (Kattai, 2003). This transport method caused separation of the material – coarser material settled at the foot of the heaps, forming the conglomerate-like structure, while finer material was flushed further, forming plateaus with the shale-like structure next to the foot of the dumps. Some of the material was left unsorted near the loading point. After 2002, a new deposition technology was implemented: water is used to wash semi-coke out of the retorts, and the moist semi-coke is transported to the landfills by trucks. The material is placed in 0.5 m thick layers that are compacted with a vibratory roller. As a result, the material does not separate and it is referred to as the well graded semi-coke type. It should be noted that the inner structure of old dumps is much more complex, as the layers of different semi-coke types do not form a regular pattern. In contrast, it can be assumed that the new parts of semi-coke landfills, which are composed of well graded semi-coke, are more homogeneous.

The shale-like type of semi-coke is distinguished from the other two types by a higher content of fines and a lower content of gravel-sized particles (Figure 1). It also had a slightly lower dry density ($0.72\text{--}0.75\text{ g}\cdot\text{cm}^{-3}$) compared to the well graded ($0.84\text{--}1.15\text{ g}\cdot\text{cm}^{-3}$) and conglomerate-like ($0.82\text{--}1.04\text{ g}\cdot\text{cm}^{-3}$) types. In all the types, the undisturbed samples showed lower dry density values than remolded samples. The lower density was a result of cementation present in the pore space of undisturbed samples, which inhibited compaction of the material. In the remolded samples, these cement bonds were mechanically broken and the material compacted spontaneously. The values of specific

gravity of solids were similar in shale-like and conglomerate-like samples – 2.22 and 2.24, respectively, but the well graded type had a somewhat higher value – 2.43.

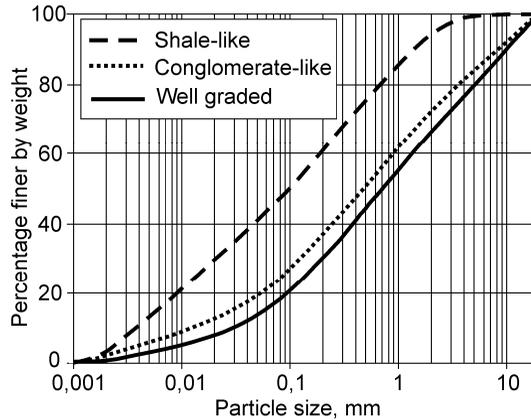


Figure 1. Average grain size distribution curves of shale-like, conglomerate-like and well-graded semi-coke samples (after Paper I – Sedman et al., 2012a).

3.1.1. Shear strength properties of semi-coke

Semi-coke consists of irregular angular particles that cause a high ratio of interlocking. The high carbonate content, dominant sand and gravel fractions and angularity of particles contribute to a high friction angle, while the content of fines, organics present in the semi-coke (up to 10%) and a high void ratio reduce it to 27–30°. Nevertheless, an exceptionally high friction angle value in the quasi-saturated conglomerate-like semi-coke was observed, reaching 39° (Figure 2). Although the shear strength of a granular material is mainly controlled by the frictional component, also cohesion plays an important role in the shear strength of semi-coke. The cohesion component in semi-coke is controlled by secondary cementation, which creates mechanical bonds between individual particles. As expected, the undisturbed samples showed higher strength values, but the testing of undisturbed samples was complicated and thus the values of friction angle and cohesion were not calculated. The remolded samples showed cohesion of 12–35 kPa (Figure 2). This indicates that even after crushing, some aggregates are bound together. Mechanical crushing of the cementing minerals begins at effective normal stresses of 600 kPa (Figure 2C), which is approximately equivalent to 50 m of overlying semi-coke. In the material buried deeper than this limit, cementation is at least partially broken, and instead, the parameters of remolded samples must be used for estimating the stability of the semi-coke deposits.

Semi-coke is petrographically and mineralogically a complex mixture that is composed of pieces of oil shale, but also contains thermally altered components. Oil shale pieces are mainly composed of calcite, dolomite, quartz, K-feldspar and clay minerals (Kattai, 2003). This part remains unchanged during disposal, but in addition, semi-coke contains altered phases, such as melilite, periclase, oldhamite and the clinker mineral belite, which have formed due to partial thermal decomposition in the final stage of retorting (Mötler et al., 2007). After disposal, hydration reactions start to occur and as a result, new hydrated mineral phases, mainly ettringite, form. The content of ettringite in the hydrated semi-coke is 11% on average (Mötler et al., 2007). Ettringite together with secondary calcite can be considered as the main source of cohesion. This contributes to the mechanical stability of the deposits, which occasionally form nearly monolithic zones.

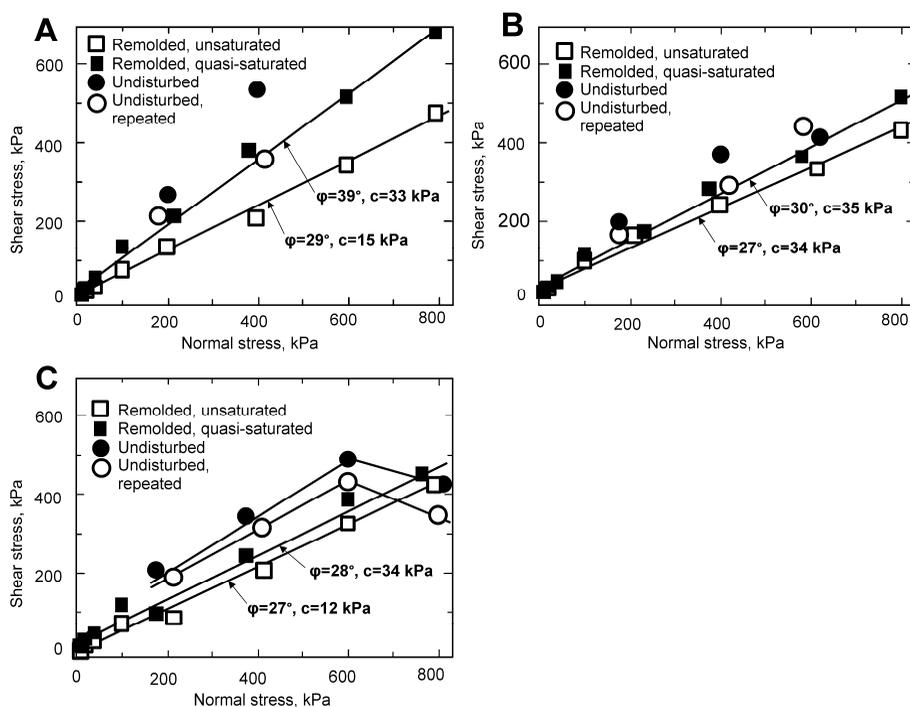


Figure 2. The average shear strength envelopes of conglomerate-like (A), shale-like (B) and well graded (C) semi-coke samples and the values of friction angle (ϕ) and cohesion (c) of remolded samples (after Paper I – Sedman et al., 2012a).

However, the cohesion from ettringite is not a stable phenomenon. Ettringite formation and stability, and therefore the geotechnical stability of the semi-coke deposits, depend strongly on the pH of the environment. Ettringite is stable in alkaline and sulfate-rich environments at pH values >10.7 , but at lower pH

values it dissolves incongruently to gypsum, aragonite/calcite, Al-hydroxide and/or Ca-aluminate type phases (Nishikawa et al., 1992; Myneni et al., 1998). Mineralogical and electron microscopy investigation of the surface samples of semi-coke deposits has indicated that under open atmospheric conditions, a sufficient pH is not attained in the ettringite stability region and the mineral decomposes (Mötlep et al., 2007, 2010). When cohesion from ettringite and/or other cementing phases disappears due to weathering, a decrease in strength can be observed. When planning disposal of semi-coke, it must be taken into account that although in the short term, semi-coke exhibits some self-cementing properties and forms nearly monolithic deposits, it is not stable in the long term. This suggests that the stability of high and steep slopes of waste heaps will deteriorate in the long run and necessary precautions should be used. In practical design, the lowest strength parameters of each semi-coke type should be applied.

3.1.2. Anomalous shear strength behavior of semi-coke

During regular geotechnical testing, an unusual phenomenon was revealed. According to common theory, soil gains additional strength appearing as increased cohesion in an unsaturated state due to tensile forces that develop between the soil particles (Fredlund and Rahardjo, 1993). Once the soil saturates, this additional strength disappears. Nonetheless, quasi-saturated semi-coke samples displayed a higher shear strength than unsaturated ones (Figure 2), which contradicts the theory of unsaturated soil mechanics. We also found that semi-coke samples reached the water-saturated state only after one week under vacuum conditions. An estimated saturation level of 0.8–0.9 was reached in the quasi-saturated samples that were used in the shear strength testing.

The unusual shear strength behavior and inhibited saturation process could be caused by the complex structure and composition of semi-coke. The concept of dual porosity (Barenblatt et al., 1960) can be applied. Semi-coke particles have high intragranular porosity. Intragranular water, e.g. water trapped in the inner pores, probably does not contribute to the additional shear strength, which depends on water films between the particles. In addition, fine irregular particles and needle-like crystallite aggregates of ettringite form a microscopically rough surface that supports water on millions of tiny projections, leaving the valleys between filled with non-wettable air capillaries. Semi-coke also showed fair hydrophobicity. This is probably caused by remains of shale oil that might cover semi-coke particles. The shale oil contains hydrophobic residual hydrocarbons (Veiderma, 2003). Hydrophobicity is known to influence the physical and hydraulic properties of soil (Bauters et al., 2000; Doerr et al., 2000). Although the geotechnical significance of the hydrophobicity is not fully understood (Hatton, 2009), it may also influence the strength properties.

Due to the described processes, the contact between the semi-coke particles' surface and water at the unsaturated state may be weaker, and as a result the formation of additional strength is inhibited. In quasi-saturated samples, a contractile skin may have formed due to a higher water content. However, when the material fully saturates, e.g. in the landfills below the permanent water table, its shear strength can probably be lower than expected, as in the fully saturated state the additional strength would disappear.

3.2. Black ash

The self-cementing behavior and related properties of black ash were studied in Paper II – Talviste et al., 2013.

Fresh black ash is a relatively well-graded material dominated by a silt fraction (Figure 3), but compared to semi-coke (Figure 1), it is finer and more uniform. The average specific gravity of solids was similar to the well graded semi-coke type – 2.43 (Paper I – Sedman et al., 2012a). The dry density value of the loose material was $1.01 \text{ g}\cdot\text{cm}^{-3}$. As some disposal methods cause grain size separation, also the properties of the fine and coarse fractions were studied. The physical properties of the fine fraction ($<125 \mu\text{m}$) were very similar to the unsorted samples – dry density was $0.97 \text{ g}\cdot\text{cm}^{-3}$ and specific gravity of solids 2.42. This is because fresh ash is dominated by particles $<125 \mu\text{m}$ which thus determine the properties of the material. The coarse fraction ($>125 \mu\text{m}$), on the other hand, was somewhat different due to a higher content of unaltered carbonates. Its specific gravity of solids was 2.62 and dry density $1.37 \text{ g}\cdot\text{cm}^{-3}$.

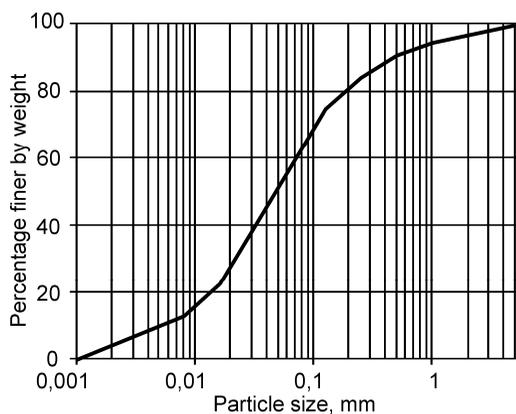


Figure 3. The average grain size distribution curve of fresh black ash (Paper II – Talviste et al., 2013).

After mixing with water, the material compacted spontaneously, and consequently, higher values of dry density were recorded. However, after initial compaction, the values of dry density did not show any systematic changes,

indicating that the development of cementation did not affect additional compaction or expansion. The dry density values during testing remained in the range of 1.18–1.33 g·cm⁻³ in unsorted ash samples, 1.15–1.27 g·cm⁻³ in the fine fraction (<125 μm) and 1.48–1.64 g·cm⁻³ in the coarse fraction (>125 μm).

3.2.1. Self-cementing properties of black ash upon application of different disposal methods

Black ash showed good self-cementing properties when mixed with water: both unsorted and fine material gained significant strength during the 90-day testing period, with compressive strength maximum values reaching 2–6 MPa, depending on the storing conditions (Figure 4). A rapid increase in compressive strength was observed in the first 30 days, but after that the growth slowed down and only slightly higher values were measured after 90 days, suggesting that strength will not likely increase significantly afterwards. Nevertheless, it is important to point out that the coarse fraction did not exhibit any cementation (Figure 4), and thus, its compressive strength can be considered to be zero for the whole testing period.

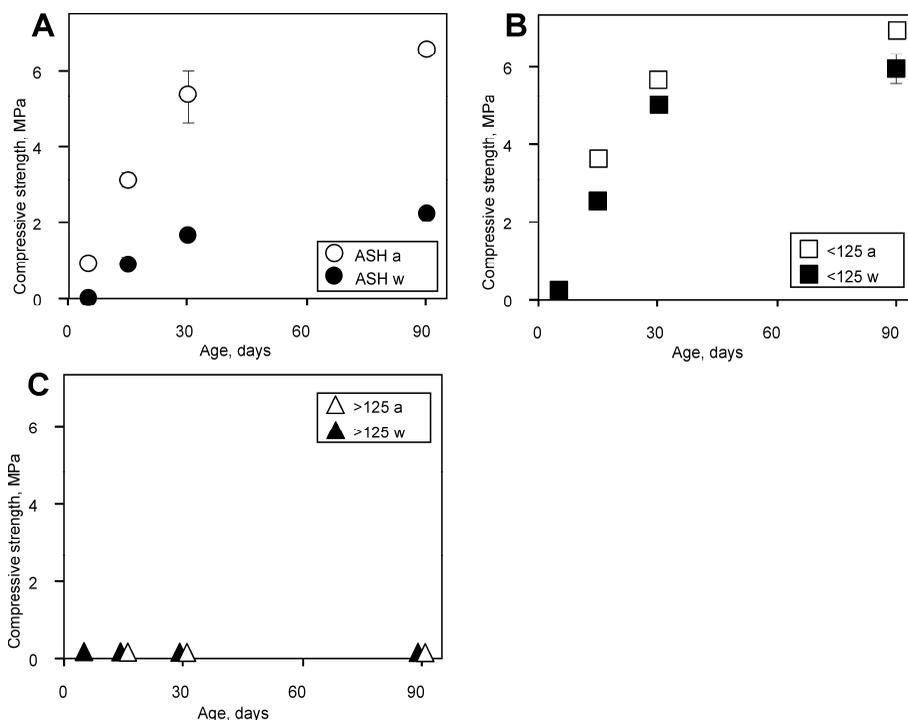


Figure 4. Compressive strength values of unsorted black ash (A), the fine fraction (B) and the coarse fraction (C) after 5, 15, 30 and 90 days. Average values and variation range (Paper II – Talviste et al., 2013).

Theoretically, black ash should be comparable to Estonian oil shale combustion ashes, especially to CFBC ash, which forms in a similar temperature range. When comparing black ash, PF and CFB ashes, it is clear that PF ash shows substantially higher self-cementing properties – the compressive strength of fly ash mortars reached 16 MPa compared to the 4 MPa strength of CFBC fly ash mortars (Arro et al., 2010). Compressive strength values of only about 1 MPa have been measured at a full scale flow channel in CFBC ash deposits (Pihu et al., 2012). These differences are expected, as the content of binding phases and consequent cementation depend on the temperatures during thermal treatment. The high-temperature PF ash (1350–1450 °C) clearly distinguishes from CFBC and black ash, which form at significantly lower temperatures (750–950 °C) (Ots, 2006). The content of binding phases in the PF fly ash reaches even 70–80%, which is more than twice as high as in CFCB ash (Kuusik et al., 2005; Bitukova et al., 2010). The compressive strength of black ash (Figure 4) is more close to CFBC ash, although it still clearly exceeds the latter's strength.

The self-cementing process has environmental benefits, because the hardened material exhibits lower permeability, and it reduces infiltration and potential leaching through the deposited waste (Adonyi and Szécsényi, 1996). It also provides stabilization of disposed waste and eliminates the need for additional stabilization methods, thus reducing disposal costs. When analyzing different disposal methods, compressive strength development should be taken into account. The coarse fraction did not exhibit any cementation during the testing period (Figure 4); thus, separation of the material during disposal should be avoided. Therefore, the hydraulic disposal with grain size separation is not the most suitable method, because the coarse fraction would produce zones with high permeability and low strength. A similar phenomenon has been described by Pihu et al. (2012), who suggest that hydraulic transport and deposition of CFBC oil shale ash is not suitable at low ash-water ratios. When the coarse fraction is not separated, the cementation is not inhibited due to a low content (approximately 25%) of the coarse fraction in the whole material. Considering this, both the dry disposal of moist material and the hydraulic transport without grain size separation seem to be suitable methods.

In addition to different self-cementing properties of grain size fractions, the cementing process is also dependant on the water saturation state of the hydrating material. When stored in water, the process is inhibited at least to some extent (Figure 4). The samples gained more strength when left in ambient air after mixing with water. When kept in water, the unsorted material gained significantly less strength, although there are no substantial differences in the mineral composition or physical properties. This phenomenon could be related to a different exposure to CO₂ and leaching behavior: CO₂ diffuses more easily into samples under ambient air conditions, favoring the carbonation reactions that increase strength. This suggests that black ash should be deposited either by dry dumping of moist material or the sedimentation pond should be drained after the disposal, because drying of initially wet deposits favors the development of cementation.

3.2.2. Mineralogy of self-cementation process

In order to evaluate the long-term stability of cemented black ash, its mineral composition was studied. Fresh black ash contained calcite (31%), quartz (15%), K-feldspar (15%) and dolomite (7%), which are also characteristic of raw oil shale. The self-cementing properties were controlled by reactive Ca phases formed during the thermal treatment of oil shale. These included the Ca-silicates belite and ferrite (8–12%), periclase (9%), free lime (3.5%) and oldhamite (4%). The average chemical composition of fresh black ash was in accordance with the mineral composition. The samples were dominated by CaO (32%) and SiO₂ (21%), but also contained MgO (8%), Al₂O₃ (5%), Fe₂O₃ (5%), K₂O (3%) and some other minor compounds. The total sulfur content was 2% and total carbon content 7%.

When fresh black ash is mixed with water, the reactive compounds start to hydrate, forming secondary cementing phases that bind the individual particles together and increase strength. The most important processes influencing the development of cementation are illustrated in Figure 5 by the changes in calcite, portlandite, belite and hydrocalumite content. The changes were more notable in the unsorted material and fine fraction, suggesting that active compounds are accumulated in the finer fraction.

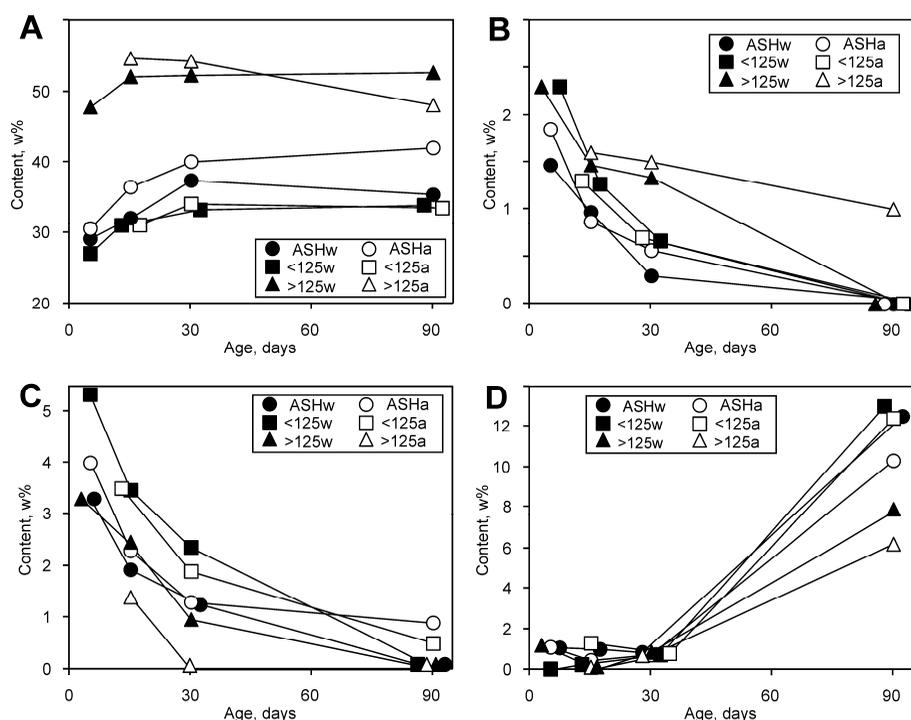


Figure 5. Changes in the average content of calcite (A), portlandite (B), belite (C) and hydrocalumite (D) under different storing conditions. Points with similar values have been shifted horizontally for clarity (Paper II – Talviste et al., 2013).

The first changes after mixing black ash with water are the slacking of free lime and the formation of portlandite, which slowly starts to carbonate to secondary calcite (Figure 5A, B). For the development of persistent cementation, the most important hydration reactions are related to belite and to a lesser extent to ferrite. The main hydration product of belite is an amorphous C-S-H gel, which cannot be detected by the XRD method, but the decreasing trend of belite content in all samples (Figure 5C) shows that at the end of the testing period, most of it had been hydrated. In addition, another binding phase – hydrocalumite – was detected by the end of testing period (Figure 5D). The composition of the cementive phase in black ash is somewhat different from other oil shale wastes: ettringite, which is a common phase in semi-coke and combustion ashes, was not detected. The analysis of cementing phases suggests that the cementation bonds in black ash are chemically stable. In the long term, the cemented deposits can be considered mechanically stable and the achieved compressive strength should not decrease significantly.

3.3. Co-deposition experiment

Mixing of two principally different wastes and properties of the resulting material was studied in Paper III – Sedman et al., 2012b.

The co-deposition of ash and semi-coke could serve as a more optimal waste management system. Ash is known to exhibit good self-cementing properties, but it is prone to cracking, which increases permeability and infiltration rates (Talviste, 2008). Semi-coke, on the contrary, does not have such good self-cementing properties, but no cracking has been observed and the hydraulic conductivity values measured in semi-coke deposits in Kohtla-Järve have stayed in the range of $1.2\text{--}3.2 \cdot 10^{-8} \text{ m}\cdot\text{s}^{-1}$ (P. Talviste, unpublished data). If mixing of these wastes could combine the good properties of both wastes, it should be more beneficial both economically and environmentally.

3.3.1. Mineral composition of semi-coke and ash mixtures

To analyze the physical processes occurring during co-deposition, mineral composition was studied. The initial mineral composition of mixtures depends on the ratio of the waste materials. Fresh PF ash contains lime, portlandite, anhydrate, calcite, quartz and several secondary Ca-silicates (Bitykova et al., 2010). Fresh semi-coke is less altered compared to combustion ash and the predominant phases are calcite, dolomite, quartz, K-feldspar and clay minerals, but in addition, also secondary phases (e.g. melilite, belite, oldhamite) can be found (Mõtlep et al., 2010). Due to the reactive secondary phases in both waste materials, the mixtures undergo mineral alteration after their disposal. The most prevalent mineral changes (Figure 6) that are responsible for the alterations in physical parameters are, firstly, the formation of stable secondary calcite

through the slacking of quicklime and its subsequent carbonation, and, secondly, the formation of ettringite and its subsequent decomposition under atmospheric conditions, which results in the precipitation of additional calcite with gypsum and Al-gel (e.g. Mötlep et al., 2007, 2010). Slacking of free lime into portlandite is completed within 48 hours (Anthony et al., 2002). This is followed by the formation of stable calcite through portlandite reacting with atmospheric CO₂, which occurs over much longer time scale (Mötlep et al., 2007). The other key mineral, ettringite, is a common secondary phase in oil shale wastes. However, it is stable only at pH values higher than 10.7, and when pH drops, it dissolves incongruently to gypsum, (amorphous) Al-hydroxide and Ca-aluminate type phases (Myeni et al., 1998). All mixtures revealed the beginning of ettringite decomposition in the uppermost 0.2–0.3 m layer after 3–4 months (Figure 6), and most of the ettringite had disappeared after one year.

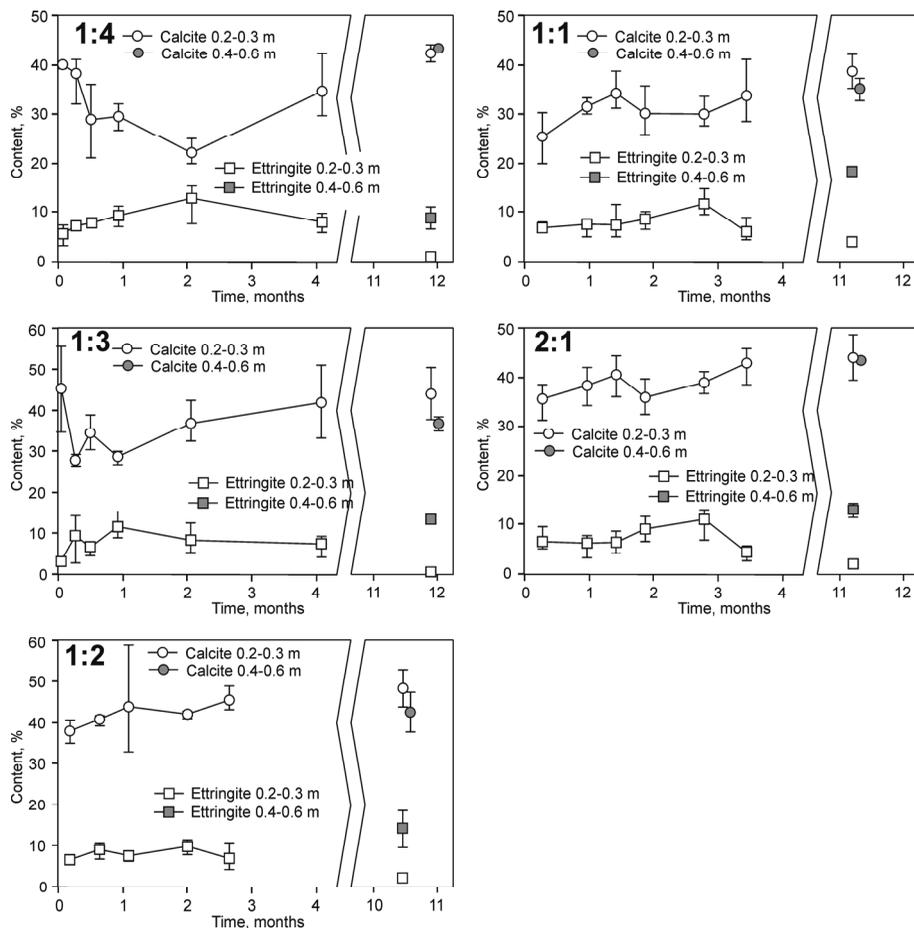


Figure 6. The content of calcite and ettringite in ash and semi-coke mixtures of 1:4, 1:3, 1:2, 1:1 and 2:1 within the first four months and after 11–12 months at different depths. Average values and variation range (Paper III – Sedman et al., 2012b).

Although the main components of mineral alteration were similar in all mixtures, the various ash and semi-coke ratios caused somewhat different behaviors. The mixtures with a high semi-coke content (1:4 and 1:3) were characterized by fast precipitation of ettringite during the first few months of the experiment, reaching 12–13% (Figure 6). After this peak, ettringite content started to decrease and instead, calcite content started to increase. In contrast, ettringite formation in mixtures with higher ash content (1:1 and 2:1) was slower and reached maximum values (10–15%) after three months from the beginning and decreased to about 5–6% only a few weeks later. Respectively, calcite content reached its maximum values at the end of the testing period when ettringite already started to decompose. The reason for these differences lies in the different ettringite formation rates in pure semi-coke and pure ash. It forms rapidly (in a week) during the hydration of semi-coke (Mötlep et al., 2007), but the process is much slower in ash, where the precipitation of well-crystalline ettringite is delayed for several weeks (Liira et al., 2009).

3.3.2. Geotechnical and physical properties of semi-coke and ash mixtures

Testing revealed that expansion and cracking processes occurred in the deposited mixtures, changing their physical properties. A decreasing trend in dry density (Figure 7) was observed in all mixtures. A lower ash content resulted in higher dry density values, because the dry density of semi-coke is greater than that of ash. Hydraulic conductivity showed a more complex evolution (Figure 7): in all mixtures, we observed a slight decrease after a few weeks from the beginning, which was then followed by an increase with an apparent peak after 3–4 months. In general, a higher ash and semi-coke ratio also caused a higher hydraulic conductivity and a more intensive expansion, with the exception of the mixture of 1:2. This mixture probably did not reach the highest permeability values, because the testing period was shorter due to the technical problems during the installation of test box. Water content indirectly indicated periods of rainy or dry weather prior to and during the testing, because peaks of precipitation coincided with increased water content in all mixtures.

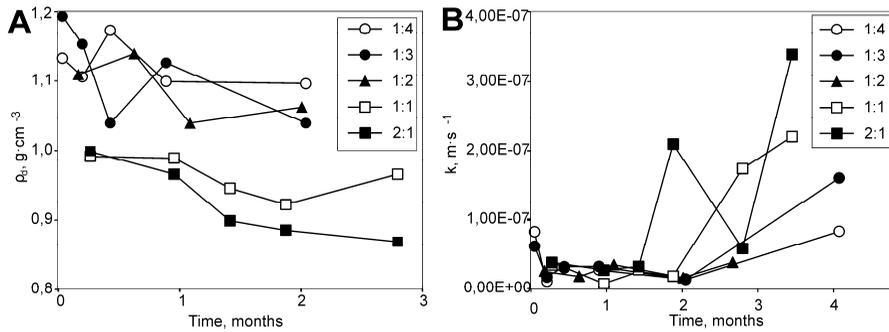


Figure 7. Changes in the average values of dry density (A) and hydraulic conductivity (B) of ash and semi-coke mixtures of 1:4, 1:3, 1:2, 1:1 and 2:1. (after Paper III – Sedman et al., 2012b).

The changes in geotechnical parameters and mineral composition are closely related to each other. The processes occurring during co-deposition are schematically explained in Figure 8. When highly porous semi-coke and fine-grained ash are mixed, the finer ash particles fill the free space between larger semi-coke particles. Initially, this guarantees lower porosity and thus contributes to lower hydraulic conductivity. This is followed by the hydration and recrystallization of unstable mineral phases, decreasing permeability even further by filling pore space.

Because the material is still soft and unconsolidated at this point, no crystallization stresses are produced (Collepari, 2003). Also, no or only little cracking occurs, because the material is plastic (Taylor et al., 2001). This is why substantial amounts (5–10%) of ettringite can be formed during early hydration without causing significant cracking. However, when material has already gained substantial strength, its free pore space comes to a critical limit. Additional ettringite formation causes cracking, because its crystallization force exceeds the strength of sediment structure (Stark and Bollmann, 1999). In the macroscopic scale, mixtures expand and as a result, dry density decreases and hydraulic conductivity increases (Figure 7). The process is more intensive in the mixtures with a higher ash content, because ash has smaller and poorly connected pores. The more porous semi-coke, on the other hand, has larger pores and the delayed ettringite formation does not cause so much expansion, because there is enough free space for secondary crystal growth. The cracking and expansion mechanism leads to higher infiltration through the deposited material, which is not a favorable property. However, if the ash proportion in the mixtures is lower, there is more free pore space for secondary crystal growth due to the high porosity of semi-coke. This suggests that in principle, co-deposition could be an alternative disposal method only at ash and semi-coke ratios lower than 1:4. This guarantees that infiltration through the co-deposited material does not exceed that of pure semi-coke deposits.

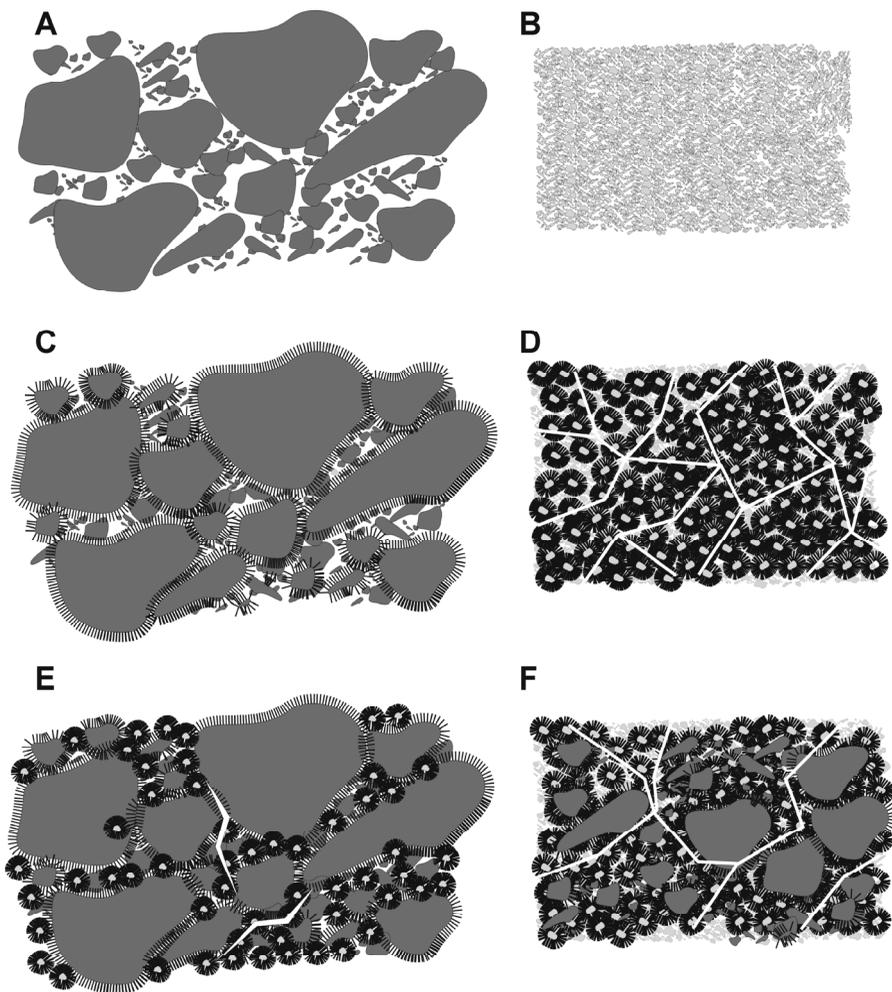


Figure 8. The expansion and cracking mechanism of ash and semi-coke mixtures. A – fresh semi-coke; B – fresh ash; C – hydrated semi-coke; D – hydrated ash with cracks; E – hydrated ash and semi-coke mixture at a low ash content; F – hydrated ash and semi-coke mixture at a high ash content. The black needle-shaped lines represent ettringite crystals and the white fissures depict the formation of cracks (Paper III – Sedman et al., 2012b).

3.3.3. Formation of a secondary enrichment zone

After 11–12 months of exposure to weather conditions, the uppermost layer (0.2–0.3 m) of all mixtures was weathered and had lost its monolithic appearance, probably mainly due to the disappearance of ettringite. Ettringite had disappeared from the uppermost 0.2–0.3 m loose layer of the mixtures with

ash and semi-coke ratios of 1:4 and 1:3, and only traces of ettringite were identified in other samples. The hydraulic conductivity of this zone was above the measuring range of used equipment. However, at a greater depth (0.4–0.6 m), we observed a strong cemented zone in all mixtures. Here, ettringite content was increased even compared to the maximum content achieved in the upper layer during the first phase of the experiment (Figure 6). We interpret this zone as a secondary enrichment zone where the carbonation of portlandite (and secondary Ca-silicate phases) is inhibited, probably due to slow diffusion of CO₂. This keeps the pH values of the pore solution at high values, supporting the precipitation of ettringite.

The hydraulic conductivity of the deeper monolithic layer (0.4–0.6 m) had low permeability in all mixtures independent of the ash and semi-coke ratio. The lowest hydraulic conductivity value ($3.36 \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$ on average) was measured in the mixture of 1:3, whereas in other mixtures the hydraulic conductivity ranged from $1.40\text{--}3.18 \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$ (on average). The reason for these low values probably lies in the formation of the secondary enrichment zone. Changes in the mineral composition and a higher ettringite content result in the reduction of pore space, thus contributing to the lower permeability. This is similar to the hydraulic conductivity reduction in the upper part of the test deposit during the first weeks after mixing. However, these low hydraulic conductivity values are only representative for this secondary enrichment zone, not for the whole mixture. It can be assumed that during large-scale disposal, when the thickness is much bigger, permeability and other properties of co-deposited material below the secondary enrichment zone remain at the range of values recorded after 3–4 months from the beginning, because the deeper zone is not influenced by surface weathering and development of the secondary enrichment zone does not reach to great depth.

4. CONCLUSIONS

Solid wastes from Estonian oil shale industry exhibit self-cementing properties when exposed to water due to calcareous reactive compounds that favor the formation of more or less monolithic deposits after disposal. This ensures that the landfilled waste is stronger and less permeable compared to the initial granular material. However, the geotechnical properties and specific behavior of different wastes are not uniform and each waste type has its limitations/problems that need to be addressed when planning their landfilling strategies.

1. The inner structure of existing semi-coke deposits is not uniform. Three structural types can be distinguished based on the deposition method – the shale-like, conglomerate-like and well graded types. These types have some differences in physical properties, mainly in grain size distribution, but differences in strength are smaller.
2. The strength properties of semi-coke are most properly characterized using shear strength, which is controlled by both frictional and cohesive components. The friction angle is between 27° and 39° , being somewhat lower than usual for calcareous sediments. The reason lies in the content of fines, presence of organics in the material and a high void ratio. Cohesion plays an important role in the shear strength of semi-coke, supporting mechanical stability of the deposits. Cohesion is probably caused mainly by the secondary cementing mineral ettringite, which forms in pores of the deposited material after disposal. However, this cementation is not stable at a lower pH range, and also mechanical crushing occurs at 600 kPa normal stress. This suggests that the stability of high and steep slopes of the waste heaps will deteriorate in the long run and in practical design the lowest strength parameters should be used.
3. The conventional saturation method in the laboratory does not guarantee a completely saturated state of semi-coke samples, and thus, those samples are considered to be quasi-saturated. This may affect the accuracy of calculated soil properties, which assume fully saturated conditions. Quasi-saturated samples showed higher shear strength than unsaturated samples. We suggest that this unusual shear strength behavior, as well as difficulties in saturating semi-coke samples, may be caused by the fair hydrophobicity of the material together with a complex inner structure.
4. Black ash, another shale oil processing waste, exhibits good self-cementing properties when mixed with water, reaching compressive strength values >6 MPa after 90 days. This makes it more similar to combustion ashes than the other oil shale retorting waste semi-coke. Most of the strength was gained during the first 30 days, and the further growth was only minor. However, the self-cementing properties are strongly controlled by the fraction of <125 μm . The coarse fraction (>125 μm) did not exhibit any cementation. The self-cementing properties are mainly controlled by the hydration of belite, precipitation of secondary calcite and to a lesser extent by hydrocalumite.

This type of cementation can be considered chemically stable. It is worth mentioning that ettringite, which is a common secondary phase in other oil shale wastes, was not detected in black ash.

5. Comparison of different storing conditions suggests that the most advantageous deposition methods for black ash are dry disposal of wet material and hydraulic disposal without grain separation, with drainage of pond after the disposal. These methods guarantee the highest compressive strength and do not inhibit the self-cementing process, which is in contrast to underwater storage. As the coarse fraction does not exhibit any self-cementing properties, hydraulic disposal in large ponds with grain size separation is not a suitable disposal method, and should generally be avoided.
6. Co-deposition of ash and semi-coke is a favorable method of wastes disposal only if the ash and semi-coke ratio is 1:4 or less. A higher ash proportion causes cracking and expansion of mixtures, leading to higher permeability. This in turn gives rise to intensive infiltration of the leachate through the material. The mineral changes causing the cracking and expansion processes are mainly governed by hydration and carbonation reactions, which result in the growth of secondary crystals, mainly ettringite and secondary calcite, in the material's pore space. If the capacity of free pore space is exceeded, intensive secondary mineralization causes expansion and cracking of the material.

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SUMMARY IN ESTONIAN

Põlevkiviõlitööstuse jäätmete tugevusomadused ja tsementeerumine

Käesolev doktoritöö uurib põlevkiviõli tootmisel tekkivate tahkete jäätmete – poolkoksi ja musta tuha tugevuse ja tsementatsiooni kujunemist ning nende omaduste seoseid ladestamisel toimuvate mineraloogiliste muutustega.

Põlevkivi on laialdase leviku ja eriilmelise koostisega settekivim, mis sisaldab bituumset orgaanilist ainet (Craig et al., 2001). Mitmete tehnoloogiliste ja kaasnevate keskkonnaprobleemide tõttu kasutatakse põlevkivi suuremahuliselt vaid üksikutes riikides, lisaks Eestile näiteks ka Brasiilias, Hiinas ning Iisraelis (World Energy Council, 2010). Üha kasvava energiavajaduse ja vähenevate naftavarude tõttu on viimasel kümnendil aga hakatud põlevkivi järele käsitlema perspektiivse tahkekütusena (Brendow, 2003).

Soodsate kaevandamistingimustega Eesti põlevkivi – kukersiit – on maailma põlevkividega võrreldes küllaltki kõrge orgaanilise aine sisaldusega, seetõttu on seda kasutatud juba üle 90 aasta. Viimastel aastatel kaevandatakse Eestis aastas 12–15 miljonit tonni põlevkivi (Statistics Estonia, 2013a), millest umbes 80% põletatakse soojuselektrijaamades ning ülejäänust toodetakse peamiselt põlevkiviõli.

Kõrge tuhasuse tõttu (ligikaudu 45–50%) kaasneb põlevkivi termilise töötlemisega paratamatult suur hulk jäätmeid, mis on eelkõige kõrge leeliselisuse tõttu liigitatud ohtlikeks jäätmeteks. Soojuselektrijaamades tekib põlevkivi põletamisel Eestis igal aastal 5–7,5 miljonit tonni põlevkivituhka, mille lisandub õlitööstusest 1–1,5 miljonit tonni jäätmeid – sõltuvalt kasutatavast utmistehnoloogiast kas poolkoksi või musta tuhka (Statistics Estonia, 2013b). Tahke soojuskandja (TSK) meetodil tekkiva jäätme (musta tuha) osakaal on siiani olnud väike, kuid kõik Eesti põlevkiviõli suurtootjad on käivitamas või juba käivitanud suure tootlikkusega TSK retorte ja seega lähitulevikus selle jäätmeliigi osakaal kasvab. Põlevkivitööstuse jäätmete taaskasutus on paraku väga väike (alla 20% tekkivast tuhast) ja suurem osa neist ladestatakse prügilatesse – tuhka tuhaplatoodele ning poolkoks spetsiaalsetesse poolkoksiprügilatesse. Musta tuhka on siiani ladestatud koos põlevkivituhaga. Kuigi koguseliselt tekib elektrijaamades põlevkivituhka praegu oluliselt rohkem, peetakse õlitööstuse jäätmeid problemaatilisemaks eelkõige suurema keskkonnoohtlikkuse tõttu, sest lisaks leeliselisusele sisaldavad need ka orgaanilisi jääke. Seetõttu on eriti oluline, et õlitööstuse jäätmete prügilad oleksid mehaaniliselt stabiilsed ja madala veejuhtivusega, et tagada nende kestvus ja minimeerida neist johtuv keskkonnamuutus. Ladestute stabiilsus sõltub muu hulgas jäätmete geotehnilistest omadustest, mida kontrollivad hüdratiseerumisel toimuvad mineraloogilised muutused.

Töö eesmärgid olid: *esiteks*, selgitada poolkoksiladestute tugevusomadusi ja sekundaarse tsementatsiooni põhjuslikku olemust ning stabiilsust, mis on

vajalik nii vanade prügilate nõuetekohaseks sulgemiseks kui ka uute ladestusalade optimaalseks planeerimiseks; *teiseks*, selgitada tahke soojuskandaja tehnoloogiat kasutava õlitööstuse jäätme, nn musta tuha tsementeerumist seoses hüdratiseerumisel toimuvate mineraloogiliste muutustega, imiteerides erinevaid ladestamise meetodeid, et selgitada välja sobivamad ladestustehnoloogiad; *kolmandaks*, selgitada poolkoksi ning tuha võimalikku kooslade tamist, uurides kokku segatud jäätmesegude veejuhtivusomadusi ning töötada välja soovitud kooslade tamise piirtingimuste määramiseks.

Poolkoks on tüüpiliselt kuni 10% orgaanilisi jääke sisaldav must erineva terasuureusega poorne materjal (Sedman et al., 2012a), mis tekib utmisprotsessides, kus soojuskandjana kasutatakse kuuma gaasi (näiteks Kiviteri tehnoloogia). Poolkoksi on aastate jooksul ladestatud Kohtla-Järvel ja Kiviõlis paiknevatesse ladestustesse rohkem kui 100 miljonit tonni (Kattai, 2003). Kuna õlitöötamises on kasutatud erinevaid tehnoloogiaid ja erinevaid ladestamise meetodeid, on poolkoksiladestute siseehitus heterogeenne. Välja saab tuua kolm struktuuritüüpi: peeneteraline kilda-laadne, jämedateraline konglomeraadi-laadne ning kaasajal ladestatav, nn. sorteerimata poolkoksi erim (Sedman et al., 2012a). Erimate tugevusomaduste varieeruvust kontrollib lõimis ning uuringust selgub, et tugevuse kujunemisel on lisaks hõrdekomponendile tähtsal kohal ka nidusus. Nidusust mõjutab tsementeerivate mineraalide, ettringiidi ja sekundaarse kaltsiidi esinemine ja jaotumine poolkoksises. Nidususkomponent pole aga püsiv, sest alates normaalpingest 600 kPa toimub tsementeerivate mineraalide mehaaniline purunemine (Sedman et al., 2012a). Samuti on poolkoksi ladestamisel vajalik arvestada, et ettringiit on kvaasistabiilne mineraal ja ta laguneb, kui pH langeb alla 10,7 (Myneni et al., 1998). Seega tuleb poolkoksiladestute pikaajalise tugevuse hindamisel arvestada piisavate varuteguritega.

Samuti selgus uuringute käigus, et poolkoksi mehaaniline käitumine veega küllastamisel on vastupidine üldlevinud teooriale: suurema veeküllastusastmega poolkoksi proovid olid tugevamad kui osaliselt küllastunud proovid (Sedman et al., 2012a). Selle ebatavalise nähtuse põhjuseks võib olla poolkoksi kerge hüdrofoobsus, mis tuleneb keerulisest poorstruktuurist ja märkimisväärsest orgaanilise ainese, sh õlikomponentide sisaldusest (Sedman et al., 2012a).

Must tuhk, teine õlitööstuse jääk, tekib utmistehnoloogiates, kus soojuskandjana kasutatakse gaasi asemel protsessis tekkivat tahket jääki (poolkoksi) (näiteks Galoter, Petroter ja Enefit tehnoloogiad). Must tuhk sarnaneb omadustelt rohkem põlevkivituhale kui poolkoksile, kuid sisaldab siiski kuni paar protsenti orgaanikat, mis annab jäätmele tumeda värvuse. Musta tuhka pole siiani eraldi ladestatud, kuid kuna TSK tehnoloogia mahud kasvavad, on tekkinud vajadus optimaalse ja ohutu ladestamise meetodi järele. Selleks imiteeriti laborikatses erinevaid põlevkivitööstuses kasutusel olevaid ladestamise meetodeid: hüdroärastust setebasseinides materjali lõimiselise fraktsioneerumise ja fraktsioneerumiseta nii pidevalt veeküllastunud kui ka kuivavates tingimustes ning niiske materjali kuivladestamist. Selgus, et must tuhk on tunduvalt

paremate tsementeeruvate omadustega kui poolkoks ning katsekehade surve-tugevus jõudis 90 päevaga kuni 6 MPa-ni (Talviste et al., 2013). Suurim tugevus saavutati fraktsioneerimata proovides, mis jäeti pärast veega segamist kuivama. Kuna musta tuha jämedamatel terasuuruse fraktsioonidel ($>125 \mu\text{m}$) puuduvad mõõdetavad tsementeerumisomadused, siis ei saa musta tuha ladestamisel kasutada hüdroärastust, eriti suures settebasseinis, kus toimub transporditava materjali lõimiseline fraktsioneerumine. Kõige sobivam ladestusmeetodid on niiske materjali kuivladestamine või hüdroärastus väiksemas settebasseinis, mis pärast materjali väljasettimist kuivendatakse (Talviste et al., 2013). Peamised mineraloogilised protsessid, mis kontrollivad musta tuha tsementeerumist, on beliidi hüdratiseerumine, sekundaarse kaltsiidi ja vähemal määral ka hüdrokalmiidi tekkimine. Ettringiiti, mis on tavaline tsementeeriva faas põlevkivijäätmetes, musta tuha hüdratiseerumisel ei moodustunud. Sellest võib järeldada, et musta tuha ladestud on tänu tsementeeriva faasi keemilisele stabiilsusele ka mehaaniliselt stabiilsemad ja säilitavad paremini monoliitse iseloomu (Talviste et al., 2013).

Siiani on põlevkivitööstuse jäätmeid ladestatud eraldi, kuid tehnoloogiliselt ja keskkonnoahutuse seisukohalt võiks nende koosladestamine olla otstarbekam. Tuhk tsementeerub hästi ja on tugevam (Arro et al., 2010), kuid kivistuvasse materjali tekivad paisumise tõttu praod, mis suurendavad filtratsioonimoodulit (Talviste, 2008). Puhas poolkoks tsementeerub halvemini ning tekkivad tsementeerivad faasid on ebastabiilsemad. Seevastu pole täheldatud pragunemist, kuna suure poorsuse tõttu on poolkoksisis sekundaarsetele faasidele rohkem ruumi. Töö kolmandas osas uuriti, kas poolkoksi ja põlevkivituhka on põhimõtteliselt võimalik koos ladestada nii, et jäätmesegu tsementeeruks paremini võrreldes poolkoksiga, kuid samas ei esineks intensiivset pragunemist. Selleks rajati välitingimustesse erineva tuha ja poolkoksi vahekorraga katsekastid ($2 \times 1 \times 0,6 \text{ m}$) ning mõõdeti segude filtratsioonimoodulit, kuivmahu-kaalu ning määrati mineraloogiline koostis. Katsete tulemusena selgus, et tuha ja poolkoksi koosladestamine on põhimõtteliselt võimalik siis, kui tuha ja poolkoksi suhe on maksimaalselt 1:4. Suurema tuhasisalduse korral on sekundaarsete mineraalide moodustumisest tingitud paisumine ja pragunemine intensiivsem, mis omakorda põhjustab filtratsioonimooduli suurenemise. Seevastu madala tuhasisalduse korral on tänu poolkoksi suurele poorsusele segus piisavalt ruumi sekundaarsete faaside mahutamiseks (Sedman et al., 2012b). Kõikides segudes on peamisteks protsessideks ettringiidi ja sekundaarse kaltsiidi moodustumine, kuid suurema ja väiksema tuhasisaldusega segud erinevad nii reaktsioonide kiiruse ja kui ka mineraalide tekke ajastuse poolest (Sedman et al., 2012b).

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