

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

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Abstract. *Oil shale ash and semicoke, solid residues from the oil shale industry, are today disposed of separately in landfills which pose a considerable environmental hazard. In the current study, the possibility of co-depositing ash and semicoke was investigated in a small-scale field experiment. The purpose of the experiment was to elucidate which mineral changes in the landfilled material occurred and how these changes affected its permeability characteristics. For this purpose five mixtures with different ash-to-semicoke ratios were prepared and placed in the open air. Changes in the dry density, hydraulic conductivity and mineral composition of mixtures were recorded within a period of four months and after one year. During the experiment the mixtures expanded and showed increased permeability due to intensive secondary mineralization. The higher the ash content of a mixture, the more intensive the expansion and, consequently, the higher the permeability, which contributed to an increased infiltration of the leachate and toxic compounds through the landfilled material, thus leading to unfavourable environmental impacts. The above suggests the possibility of co-depositing ash and semicoke, but only if the ash content of their mixture is low enough.*

Keywords: *oil shale ash, oil shale semicoke, hydraulic conductivity, mineral composition.*

1. Introduction

Oil shale is an organic-containing sedimentary rock that is widely spread all over the world. Its effective and sustainable usage is, however, complicated

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due to the high amount of solid waste (40–85% of the fuel) remaining after the processing. The large-scale exploitation of oil shale is common practice in Estonia where kerogenous oil shale (kukersite) is burnt in thermal power plants to produce heat and electricity, as well as retorted to produce shale oil [1]. The main residues from the oil shale industry are oil shale ash (hereinafter ash) and semicoke. At the current production rate each year 5–7 Mt of ash and nearly 1 Mt of semicoke are formed in Estonia [2].

Ash is a light-coloured mineral material which remains after incinerating oil shale in thermal power plants for heat and electricity generation. In the plants, the temperatures in pulverized firing (PF) boilers reach about 1300 °C and in circulating fluidized-bed (CFB) boilers, 700–850 °C [1]. This ensures that all of the organic matter contained in oil shale is burnt out. Due to such high temperatures also significant changes in the mineral composition of ash occur, namely abundant free lime (CaO), Ca-silicate and Ca-sulphate phases are formed [3–5]. Fly ash is mainly composed of silty and bottom ashes of the sandy fraction, but during landfilling these ashes get mixed. Most of the ash is deposited employing the wet method of disposal in slurry with a water-to-ash ratio of 20:1 (hydraulic transport). Due to its high content of free lime and other reactive phases, ash has self-cementing properties and thus forms a weakly lithified mass, so-called ash rock, after disposal.

Two methods are used to produce shale oil, namely the vertical gas generator process (i.e. the Kiviter process) and the solid heat carrier process (i.e. the Galoter process). Semicoke results as a solid residue from the Kiviter process, whereas the Galoter process yields a residue called black ash. The latter is similar in composition to ash, but contains up to a few per cent of unburnt organic material in addition. The temperature in the Kiviter process reaches 350–400 °C [6, 7], but in the last stage of the retorting process semicoke is heated to 900 °C in aerobic conditions to burn out as much of the organic material as possible [8]. However, the residence time of the combustion stage is short which does not guarantee the complete decomposition of organics. As a result, the retorting residue contains 6–10% of organic material in addition to the mineral matter. Due to the presence of organics semicoke is highly porous as pointed out by Külaots *et al.* [9]. Its mineral part contains predominantly phases that are characteristic of raw oil shale [10, 11]. Fresh semicoke contains only trace amounts of free lime, oldhamite, anhydrite and minor secondary Ca-silicate phases that have been formed due to the partial thermal decomposition of semicoke and the reactions taking place in the final stage of combustion [10]. Semicoke may be defined as a coarse-grained poorly sorted material containing all grain-sized fractions from gravel to clay with sand as a dominating one. Due to its low content of reactive phases and high content of organics the self-cementing properties of semicoke are much less pronounced than those of ash.

Ash and semicoke are both considered hazardous wastes [12] mainly due to the high alkalinity of the leachate water and, in addition, the presence of organic compounds in semicoke. Secondary applications of both types of

waste are currently insignificant (less than 5%) and these are mostly land-filled. The landfills represent a major source of pollution in Estonia, because the alkaline leachate and toxic compounds (e.g. PAHs, oil residues) infiltrate through the deposits into the environment. One way to reduce the risk of contamination is to diminish leachate formation by lowering the permeability of the landfill body.

Currently ash and semicoke are deposited separately in landfills, using different technologies of dumping. As long as we have no good alternatives to disposal, the landfills must be designed and constructed as environmentally safely as possible. Landfill design and methods of deposition should ensure the low permeability of the landfill body to minimize the infiltration of the leachate into the surrounding soil and groundwater, and the consequent pollution of the environment. Although ash has good self-cementing properties, recent studies [13] have shown that the inner structure of ash deposits is not uniform and thus the landfilled material's physical properties, such as strength, density and permeability, may vary significantly. This study demonstrated that ash deposits indeed contain low permeability zones (hydraulic conductivity $0.15\text{--}16.1\cdot 10^{-9}\text{ m}\cdot\text{s}^{-1}$), but these zones are spread discontinuously. Moreover, the overall permeability of ash deposits is relatively high because the ash is cracked and water flows in the system of vertical and horizontal cracks [14]. As a result, the leachate can easily penetrate through the cracks into the soil and groundwater. Semicoke deposits, on the contrary, contain no cracks and the permeability of the deposited material remains low. At present semicoke is deposited using the solid method of disposal. The material is transported to landfills by trucks and is disposed of in 0.5 m compacted layers that are levelled to construct the slope ratio of 1:6. This slope ratio and the low values of hydraulic conductivity ($10^{-8}\text{ m}\cdot\text{s}^{-1}$) of the compacted and hydrated semicoke should minimize the infiltration of the leachate through the deposit. Due to the limited space for landfills and application of the solid heat carrier technology, it is foreseen that in the future both types of waste will be disposed of together in the same landfill, which can influence the permeability and other physical properties of the deposited material.

The specific goals of this research were, firstly, to study the hydration and carbonation reactions and corresponding changes in the physical properties, such as permeability and density, of landfilled ash and semicoke mixtures at different ratios in a small-scale field experiment; and, secondly, to give a preliminary estimate of co-deposition as an alternative method of disposal, based on the permeability characteristics of the landfilled material.

2. Materials and methods

The field experiment was conducted in the semicoke landfill operated by Viru Keemia Grupp (VKG) near the town of Kohtla-Järve, northeast

Estonia. In the company both types of waste – ash and semicoke, result from burning and processing oil shale, respectively, and have been deposited separately so far.

For experiments five mixtures of wastes with different ash-to-semicoke ratios (1:4, 1:3, 1:2, 1:1 and 2:1, by volume) were prepared by mechanically mixing the materials, placed in wooden boxes measuring 2x3x0.6 m each, and compacted using a portable vibratory plate compactor. As samples fresh moist semicoke from the Kiviter-type retort, VKG, and fresh dry ash from the PF generator, Põhja Soojuselektrijaam of VKG Energia, served. The boxes with the mixtures were put in the field in the open air on May 15, 2008 (mixtures 1:4 and 1:3) and on June 3, 2008 (mixtures 1:1 and 2:1) for a period of four months. Due to an unsatisfactory mixing of ash and semicoke in the test box containing the 1:2 mixture, a new box with freshly mixed wastes was placed in the field on June 28, 2008.

During the experiment the hydraulic conductivity (k), dry density (ρ_d), water content (w) and mineral composition of mixtures were determined after one, two and four weeks, and two and four months. The weather data were recorded at Jõhvi automatic weather station, Estonian Institute of Meteorology and Hydrology, which is situated about 13 km southeast of the testing site.

The hydraulic conductivity of mixtures was measured *in situ* in pre-drilled holes (diameter 30 mm) at a depth of 0.2–0.3 m by using a GeoN Permeameter Pi301 falling-head permeability testing device. Undisturbed samples from each mixture were collected at the same depth for dry density and water content determinations which were carried out at the Geotechnical Laboratory, Estonian Environmental Research Centre. The mineral composition was determined by X-ray powder diffractometry (XRD) at the Department of Geology, University of Tartu. The boxes with samples were closed air-tightly on the spot and the latter were analysed within 24 h (in a few cases within 48 h) to prevent further transformation. The quantitative mineral composition was determined using a Siroquant 2.5 code [15]. Each test was performed with three (in some cases two) samples in parallel. A Zeiss-DSM 940 Scanning Electron Microscope (SEM) was employed to study and photograph the micromorphology and inner structure of unmixed ash and semicoke samples. The samples were coated with conductive gold layer prior to SEM analyses. An integrated energy dispersive analyzer (EDS) was used to determine the composition of the secondary minerals formed in the pore space of the material.

An additional measurement of hydraulic conductivity was undertaken in 11–12 months from the beginning of the experiment after the mixtures had been exposed to the weather for the same period of time. The hydraulic conductivity was measured below the uppermost weathered layer of the material at a depth of 0.4–0.6 m. In addition, the mineral composition of the material was analysed at a depth of 0.2–0.3 and 0.4–0.6 m after 11–12 months.

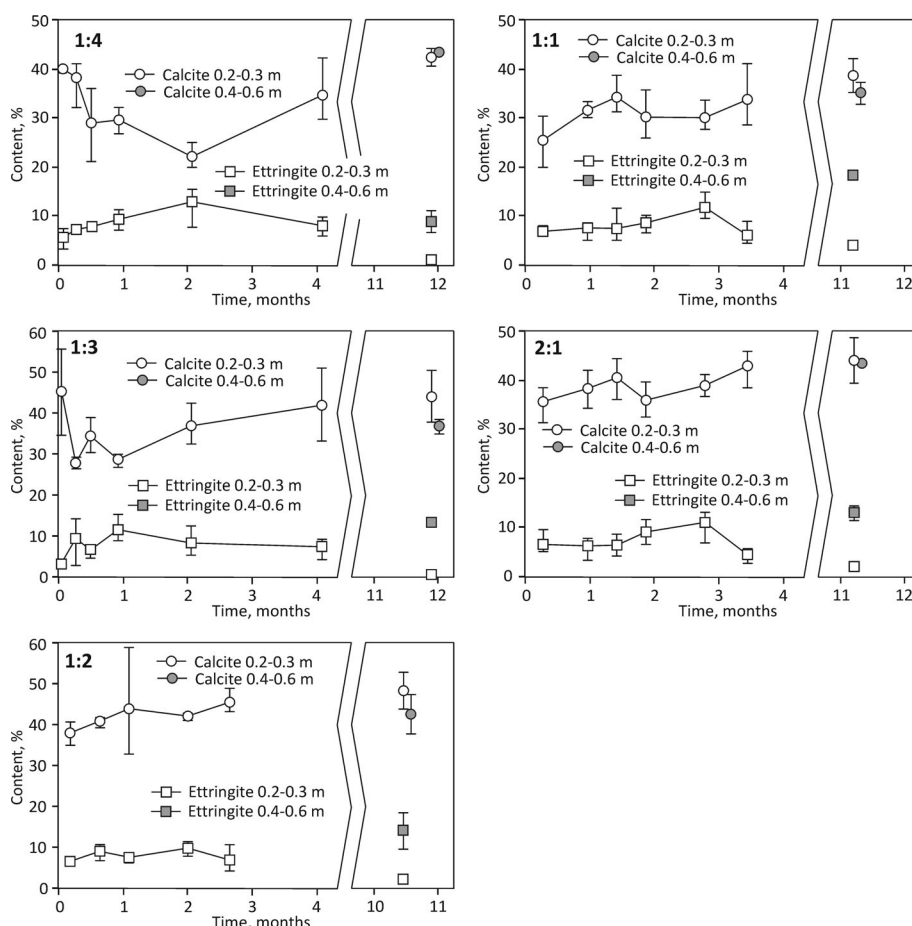


Fig. 1. The content of calcite and ettringite of ash and semicoke mixtures 1:4, 1:3, 1:2, 1:1 and 2:1 within the first four months and after 11–12 months at different depths (averaged values and error bars).

Altogether 71 samples were taken for determination of physical parameters and 102 samples were taken and analyzed for mineral changes. Also, 105 hydraulic conductivity tests were performed.

3. Results and discussion

3.1. Mineralogy

All the mixtures are dominated by the presence of calcite, portlandite, quartz, K-feldspar, and also secondary Ca-silicate and Ca-sulpho-aluminate phases, which are either characteristic of ash, semicoke or both. After mixing the material undergoes progressive hydration and subsequent carbonation which are responsible for the formation of secondary phases in the pore

space that modifies the hydraulic conductivity of the solidified sediment. The major mineral changes are, firstly, the formation of stable calcite through the slacking of quicklime and its subsequent carbonation and, secondly, the formation of Ca-sulpho-aluminate type phases, mainly ettringite, and the subsequent decomposition of the latter under atmospheric conditions that results in the additional precipitation of calcite, gypsum and Al-gel [5, 10].

The slacking of lime (quicklime) is completed in 48 hours [16]. The process is followed by the formation of stable calcite through the reaction of portlandite with atmospheric CO₂. The latter reaction lasts for months or even years due to the slow diffusion controlled transport of CO₂ into the sediment, and is further retarded due to the intensive precipitation of calcite and other secondary minerals that gradually block out the pore space [5].

Another key mineral, ettringite, is a common secondary mineral phase that is formed during the hydration of semicoke and ash in alkaline conditions as a result of the reaction of portlandite with sulphur compounds (oldhamite (CaS) in semicoke and anhydrite (CaSO₄) in ash) and dehydroxylated aluminosilicate clays and/or Al-Si glasses.

Depending on their ash-to-semicoke ratio, the mixtures behaved somewhat differently (Fig. 1).

The mixtures 1:4 and 1:3 were characterized by the fast precipitation of ettringite during the first few months of the experiment (Figure 1). Their maximum content of crystalline ettringite reached 12–13% after one to two months. After having reached this peak, the ettringite content started to decrease and that of calcite began to increase during the second phase of the reactions.

The higher ash mixtures (1:1 and 2:1), however, behaved differently from the previous scenario (Fig. 1). In these mixtures the ettringite formation was much slower and reached maximum (10–15% of the crystalline phase) after three months from the beginning of the experiment and decreased to about 5–6% only a few weeks later. Respectively, the calcite content reached maximum at the end of the testing period when ettringite already started to decompose. The behaviour of the 1:2 mixture was more similar to the latter scenario, but its mineral changes were not as drastic, e.g. the ettringite content remained mostly below 10% during the whole experiment, whereas that of calcite increased from about 38% in the beginning up to only 43% at the end of the test period (Fig. 1).

The pattern of mineral changes in the mixtures is quite different from that in unmixed ash and semicoke because the formation of ettringite in the latter takes place at different rates. Ettringite is formed rapidly (within a week) during the hydration of semicoke [10], while Liira *et al.* [17] have shown that the process is much slower in ash where the precipitation of the highly crystalline ettringite is delayed for several weeks. This was explained by the inhibited crystallization of ettringite needles like crystallites at high pH values of the pore solution [17].

The mineral reactions taking place in the mixtures of semicoke and ash follow the same sequence. The fast crystallisation of ettringite, which is characteristic of semicoke, takes place in low ash mixtures (1:4, 1:3), while the slow ettringite crystallization is observed to take place in high ash mixtures (1:1 and 2:1).

In all experiments ettringite started to decompose in the uppermost 0.2–0.3 m layer after three to four months (Fig. 1). According to Myneni *et al.* [18] ettringite is stable at the pH values of the pore solution higher than 10.7, but dissolves incongruently to gypsum, (amorphous) Al-hydroxide and Ca-aluminate type phases at the lower pH values of the pore solution. Under the influence of atmospheric CO₂ ettringite has been found to decompose into Ca-sulphate, Al-gel and calcium carbonate [20] due to the decrease of the pH of the pore solution. This agrees well with our observations that the content of calcite and gypsum (CaSO₄) increased after the ettringite decomposition had started.

At the beginning of the experiment with higher ash mixtures the ettringite decomposition in the upper part of the deposited material causes an increase in the calcite content. The lime content of PF ash may be as high as nearly 20% [4]. The content of free lime and, respectively, of portlandite in the mineral part of semicoke is less than 1% [10] and most of the newly formed Ca-carbonate is precipitated during the ettringite decomposition.

This also means that the lower content of free lime and, respectively, of portlandite in semicoke causes, compared to the deposited ash, the faster decomposition of ettringite as the pH of the pore solution quickly drops below its stability limit (<10.7).

The decomposition of unstable secondary pore-filling phases was noticed in the samples taken after approximately one year (Fig. 1). Ettringite had disappeared in the uppermost 0.2–0.3 m loose layer of mixtures with ash-to-semicoke ratios of 1:4 and 1:3, and only its traces were detected in the other samples. However, at a greater depth (0.4–0.6 m) we observed a distinct cemented zone where the ettringite content in all the mixtures was even higher than its maximum in the upper layer during the first phase of the experiment (Fig. 1). In the authors' opinion this zone is a secondary enrichment area where the carbonation of portlandite, and secondary Ca-silicate phases, is inhibited probably due to the slow diffusion of CO₂. This keeps the pH values of the pore solution high which favours the precipitation of ettringite.

3.2. Geotechnical parameters

Changes in the geotechnical parameters of mixtures during deposition are closely related to those in their mineral composition and thus also highly depend on ash-to-semicoke ratio. In general, after three to four months the dry density had notably decreased compared to its values at the start of the experiment (Fig. 2). This decrease indicates that the landfilled material undergoes significant expansion whose extent increases with increasing ash

content of the mixture. The ash-to-semicoke ratio also had an effect on the absolute values of this parameter. Namely, the lower ash content resulted in higher dry density values, because the dry density of semicoke is higher than that of ash. The maximum initial dry density values, 1.13 and 1.19 $\text{g}\cdot\text{cm}^{-3}$ on average, were recorded in the mixtures 1:4 and 1:3, respectively, while the lowest initial values, 0.99 and 1.00 $\text{g}\cdot\text{cm}^{-3}$, were recorded in the mixtures 1:1 and 2:1, respectively.

The change of the water content (Fig. 2), however, was not as distinct over the test period, being dependent on both weather conditions and the physical properties of the material. It indirectly denotes periods of rainy or dry weather prior to and during the testing (Fig. 4). The higher peaks of precipitation coincided with the increased water content in all the mixtures.

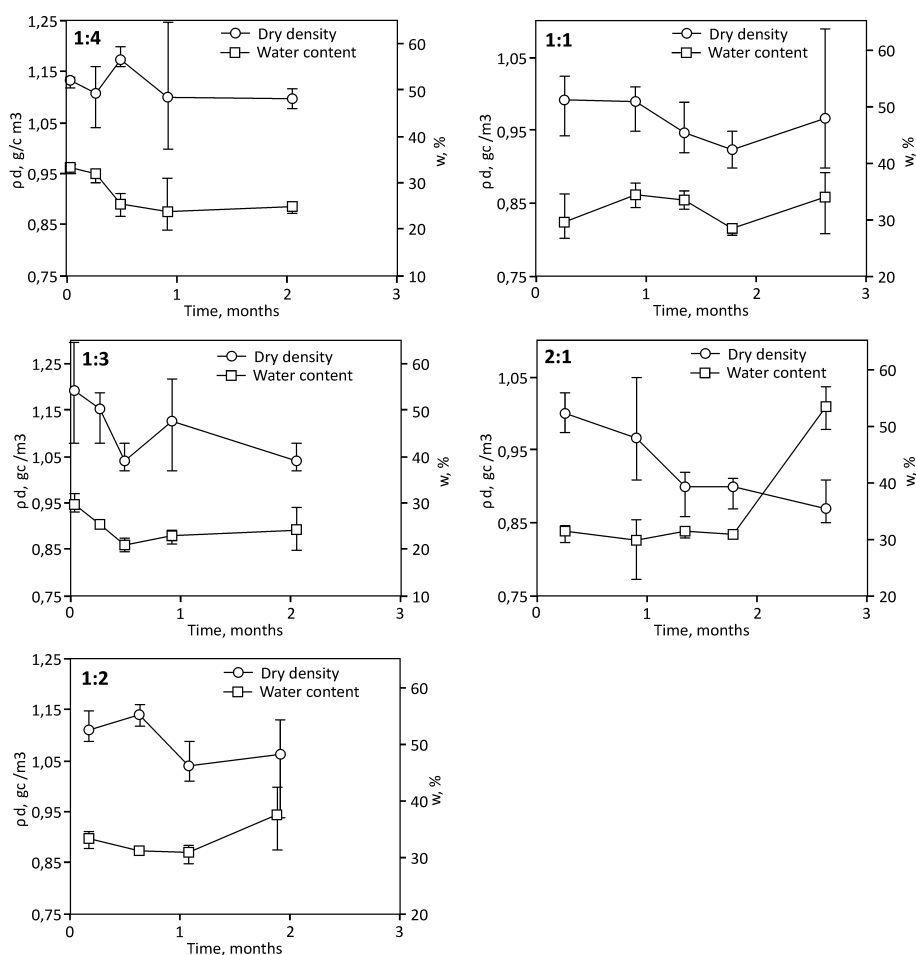


Fig. 2. Changes in the dry density and water content of ash and semicoke mixtures 1:4, 1:3, 1:2, 1:1 and 2:1 within the first three months (averaged values and error bars).

In contrast, the hydraulic conductivity of mixtures showed a more complex dynamics (Fig. 3). Its slight decrease in all the mixtures was observed after a few weeks (one to four) from the beginning of the experiment, which was then followed by an increase with an apparent peak after three to four months. In general, the higher ash-to-semicoke ratio led to the higher hydraulic conductivity, except for the mixture 1:2, whose testing period was shorter than those of the other mixtures and whose permeability values probably remained low during the testing.

Changes in the dry density and hydraulic conductivity of mixtures correlated quite well: the hydraulic conductivity increased with decreasing dry density (Figures 2, 3). Hydraulic conductivity is a property of a porous

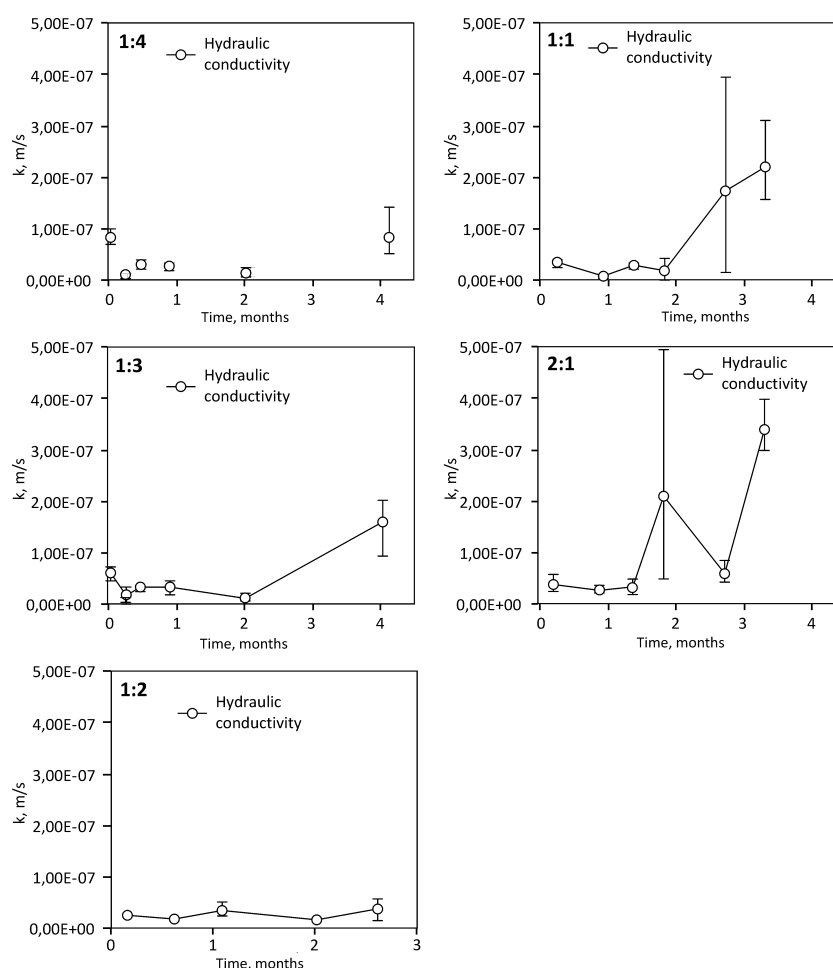


Fig. 3. Changes in the hydraulic conductivity of ash and semicoke mixtures 1:4, 1:3, 1:2, 1:1 and 2:1 within the first four months (averaged values and variation bars).

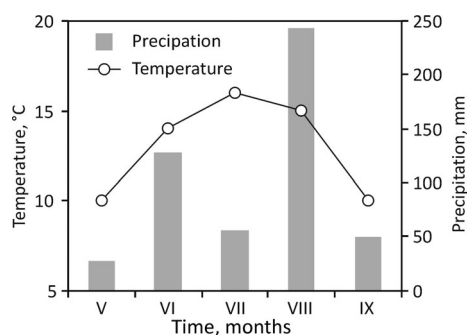


Fig. 4. The monthly average temperature and precipitation recorded at Jöhvi automatic weather station, Estonian Institute of Meteorology and Hydrology, 13 km southeast of the testing site.

medium that depends on pore size, distribution, and connectivity. The pore space in mineralogically and geochemically unstable semicoke and ash sediments is significantly modified due to the secondary mineral precipitation, recrystallization and dissolution processes. Generally, the secondary mineralization causes the loss of the pore space and, as a result, the decrease of hydraulic conductivity. This process was observed to take place during the first phase of the experiment (the first four weeks) when the hydraulic conductivity values were lowered (Fig. 3). However, after this decrease these values started to rise and in three to four months had increased rapidly in high ash mixtures (1:1 and 2:1) by nearly an order of magnitude. This increase, although less marked, was also noticed in lower ash mixtures. This process was accompanied by the expansion of the material (the decrease of dry density) (Fig. 2). Both of these changes are probably caused by the formation of microcracks in the solidified material, which coincided with the most intensive period of ettringite formation. This suggests that the development of cracks in the mixtures under study is related to the delayed ettringite formation in concrete or mortar type materials [19, 20].

After 11–12 months of exposure to the weather the uppermost layer (0.2–0.3 m) of all the mixtures was weathered and had lost its monolithic appearance, probably mainly due to the disappearance of ettringite. However, an additional testing showed that in the deeper monolithic layer (0.4–0.6 m) below the uppermost weathered layer of the material low permeability values were measured in all the mixtures independent of their ash-to-semicoke ratio. The hydraulic conductivity of the mixture 1:3 was the lowest, $3.36 \cdot 10^{-9} \text{ m} \cdot \text{s}^{-1}$ on average, whereas that of the other mixtures varied from $1.40 \cdot 10^{-8}$ to $3.18 \cdot 10^{-8} \text{ m} \cdot \text{s}^{-1}$ on average. The reason for this probably lies in the formation of the secondary enrichment zone in the deeper part of the test deposit. The mineral changes in and higher ettringite content of mixtures result in the diminishing of the pore space, thus contributing to the lower permeability, similarly to the decrease of hydraulic conductivity in the upper part of the test deposit within the first weeks of the experiment. How-

ever, these low hydraulic conductivity values are characteristic of mixtures in the secondary enrichment zone only, not of all the mixtures.

Changes in its geotechnical properties, especially in hydraulic conductivity, are strongly related to the mineralogical processes occurring in the deposited material, ettringite formation being probably the most important. The latter may be divided into two stages: primary and secondary (or additional). The primary ettringite formation during the initial hydration of sediments does not lead to cracking, because crystallization occurs yet in the unconsolidated soft sediment matrix, and thus no expansion stresses are produced [20]. However, if the sediment is already hardened, e.g., by carbonation and late sulphate release from the dissolution of gypsum, etc. [21], then an additional ettringite formation may lead to the development of cracks. The ettringite crystal growth (crystallization pressure) or increase in volume causes stresses which exceed the tensile strength of the sediment structure and can therefore cause the cracking of the material [22]. Moreover, the pH of the pore solution in the mixtures of ash and semicoke is, depending on temperature, between 12.5 and 13 due to the portlandite equilibrium. This means that the primary ettringite, which is uniformly formed in the soft sediment, is highly microcrystalline [22]. At the later stages of the experiment when the sediment has solidified, this uniformly distributed ettringite may cause expansion due to the adsorption of water on tiny ettringite crystals. This may lead to the cracking of the material if the tensile strength of the sediment microstructure is exceeded [21]. On the other hand, the pH of the pore solution in the upper layer of the sediment is lowered due to the carbonation reactions and microcrystalline ettringite can be recrystallized into large, fibre-shaped crystals that are formed at the pH values of 10–12 [23]. This may also incite expansion forces. Moreover, small crystals are inherently unstable compared to larger ones because of their greater surface area, and thus ettringite formed as small crystals in a paste tends to recrystallize in any voids or cracks that may exist in a sediment [19].

The sediment microstructure is another factor which influences expansion due to the formation of ettringite. Taylor *et al.* [19] have pointed out that the expansion is lessened or eliminated if the material is plastic. This is why substantial amounts (5–10%) of ettringite can be formed during an early hydration without causing significant expansion and only a decrease in hydraulic conductivity may be observed. The availability of the free pore space comes into play when the material has already gained substantial strength due to the secondary mineralization. The uniaxial compressive strength of the hydrated PF ash sediment may reach 10 MPa [24] due to the carbonation and hydration-recrystallization of secondary Ca-silicate phases that control the pozzolanic properties of ash [25]. In contrast, the hydration and solidification of the semicoke sediment results in the uniaxial compressive strength of about 1.2 MPa on average (Peeter Talviste, unpublished data). If the material is porous and there is much space between its particles, then ettringite is deposited in a freely available space and does not contribute

to expansion. But if the pores in which ettringite is deposited are small and poorly connected, the delayed ettringite formation produces more expansion [19]. Semicoke is a coarse-grained poorly sorted material with high porosity. Its pore space is dominated by large ($>50\text{--}100\ \mu\text{m}$) interconnected pores that are filled with the sparsely spaced elongated crystal aggregates of ettringite (Fig. 5). Ash, on the contrary, is a fine-grained material with more than 50% of particles with a grain size $<0.1\ \text{mm}$ in total ash and $>60\%$ of particles with a grain size $<10\ \mu\text{m}$ in fly ash [1]. As a result, the delayed ettringite formation in porous semicoke causes no expansion, because there is enough free space for secondary crystal growth, but in ash with small and poorly connected pores its formation and hydration have a significant influence on expansion because the available pore space is limited due to smaller porosity. That is why an intensive cracking and consequent expansion are more likely to take place in higher ash mixtures.

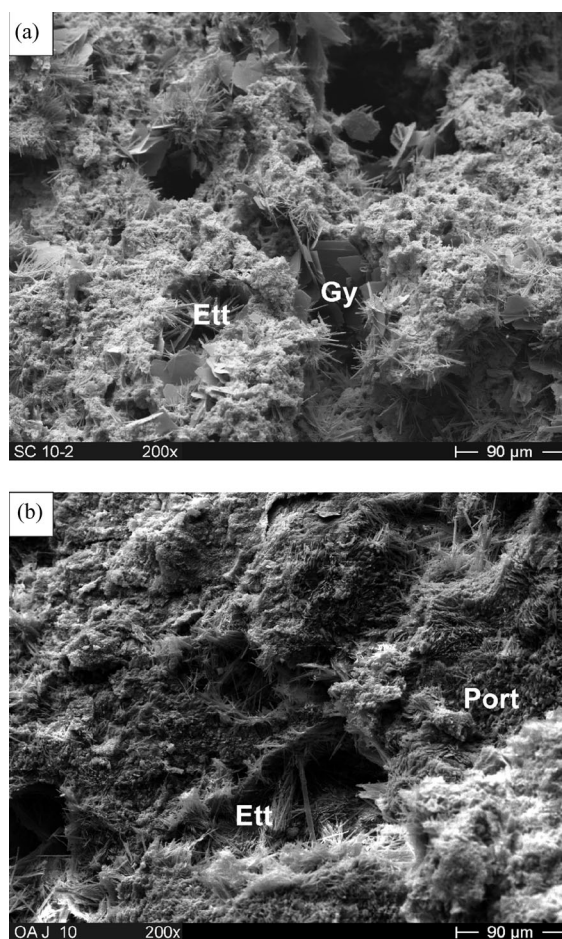


Fig- 5. SEM photograph of hydrated semicoke (a) and ash (b). Ett – ettringite, Gy – gypsum, Port – portlandite.

The expansion and cracking mechanisms are schematically illustrated in Fig. 6. When the highly porous semicoke and fine-grained ash are mixed, the finer ash particles fill the free space between the larger particles of semicoke. At the beginning this guarantees the lower porosity of mixtures and thus leads to lower hydraulic conductivity. This is further followed by the hydration and recrystallization of unstable mineral phases and precipitation of secondary minerals that additionally decrease permeability by filling the pore space of the material. Although semicoke is highly porous, at some moment its free pore space attains a critical limit and the crystal growth capacity is exceeded causing cracking due to the crystallization force. On a macroscopic scale the mixtures expand and, as a result, dry density decreases and hydraulic conductivity increases (Fig. 6). This process is most notable in higher ash mixtures which also contain more lime and are thus more prone

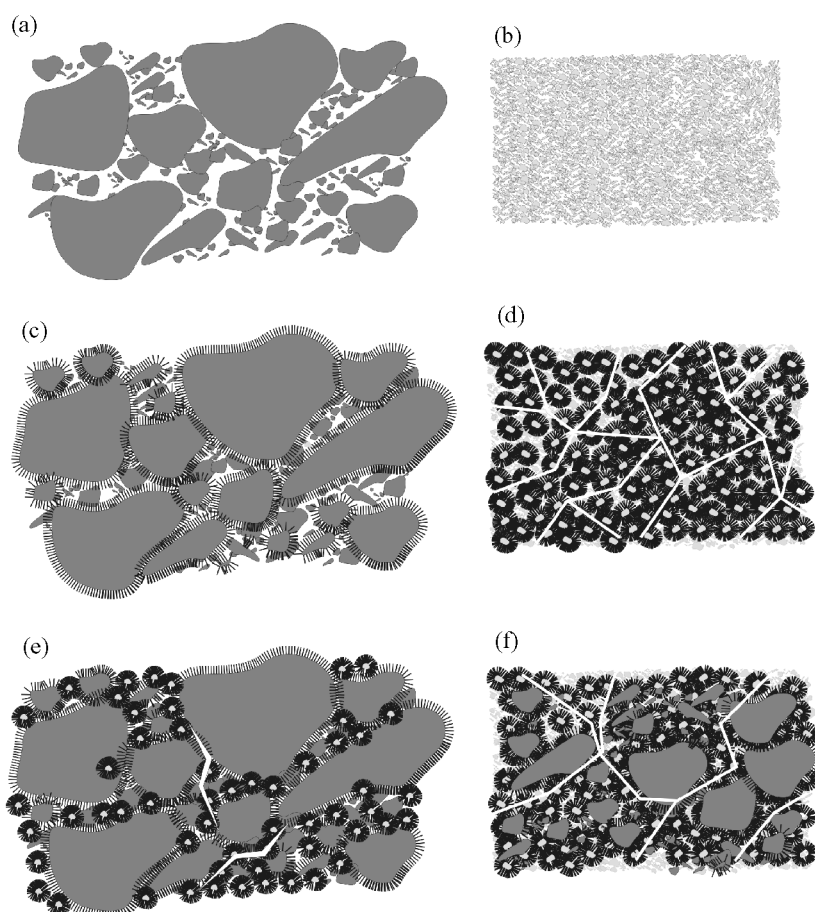


Fig. 6. Expansion of ash and semicoke mixtures. Fresh (a) and hydrated (c) semicoke; fresh (b) and hydrated (d) ash; mixture of ash and semicoke at low (e) and high (f) ash content. The black needle-shaped lines represent ettringite crystals and the white fissures picture the formation of cracks.

to expand and form cracks as well. This leads to a more intensive infiltration through the deposited material, which is highly disfavoured in any waste deposit. However, if the ash proportion of the mixture is lower, there is more free pore space for the secondary crystal growth due to the high porosity of semicoke. As a result, fewer cracks are formed and hydraulic conductivity values remain lower than in higher ash mixtures, being comparable to those of the separately landfilled semicoke. This suggests that, in principle, the co-deposition of ash and semicoke is possible, but only if their ratio in the mixture is lower than 1:4. This should guarantee that the intensity of infiltration through the landfilled material is not more intensive than in semicoke deposits. So, co-deposition can be considered, at least theoretically, an alternative method to the current modes of wastes disposal. However, before implementing this technology, pertinent large-scale tests with the application of the results of this study will be needed.

4. Summary

The study of the deposited mixtures of ash and semicoke demonstrated that mineral changes therein are mainly governed by hydration and carbonation reactions, which results in the growth of secondary crystals, mainly ettringite and secondary calcite, in the landfilled material's pore space. On the one hand, during this process the pores will be physically filled up and narrowed and thus hydraulic conductivity will be decreased. On the other hand, if the capacity of the free pore space is exceeded, an intensive secondary mineralization causes the expansion and cracking of the material which leads to its higher permeability. A critical factor which affects the abovementioned two controversial processes seems to be ash content of mixtures, because cracking and expansion were most notable in higher ash mixtures.

When considering the environmental benefits of co-deposition, one must take into account the potential infiltration of the leachate through the deposited wastes. The permeability of the separately deposited semicoke is lower than that of ash. So, the latter expands and, as a result, cracks are formed therein. This in turn leads to an intensive infiltration of the leachate through the material. When co-depositing the two wastes it must be ensured that the permeability and subsequent infiltration through the landfilled material should not be more intensive than in the semicoke deposit alone. The study indicated that if the mixture's ash-to-semicoke ratio was higher than 1:4, the permeability was not low enough to regard co-deposition as a more favourable method of wastes disposal. The higher permeability of the material does not guarantee its sufficient isolation capacity which is required for construction of impermeable layers of deposits. However, the problem can be overcome by decreasing the disposable mixture's ash-to-semicoke ratio to 1:4 or lower which should enable expansion and permeability to be maintained low as is characteristic of semicoke deposits.

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REFERENCES

1. Ots, A. *Oil Shale Fuel Combustion*. Tallinn, Tallinna Raamatutrükikoda, 2006.
2. *Statistical Yearbook of Estonia*. Tallinn, Statistics Estonia, 2010.
3. Kuusik, R., Uibu, M., Kirsimäe, K. Characterization of oil shale ashes formed at industrial-scale CFBC boilers. *Oil Shale*, 2005, **22**(4S), 407–419.
4. Bitjukova, L., Mõtlep, R., Kirsimäe, K. Composition of oil shale ashes from pulverized firing and circulating fluidized-bed boiler in Narva Thermal Power Plants, Estonia. *Oil Shale*, 2010, **27**(4), 339–353.
5. Mõtlep, R., Sild, T., Puura, E., Kirsimäe, K. Composition, diagenetic transformation and alkalinity potential of oil shale ash sediments. *J. Hazard. Mater.*, 2010, **184**(1–3), 567–573.
6. Kann, J., Elenurm, A., Rohtla, I., Golubev, N., Kaidalov, A., Kindorkin, B. About thermal low-temperature processing of oil shale by solid heat carrier method. *Oil Shale*, 2004, **21**(3), 195–203.
7. Koel, M. Estonian oil shale. *Oil Shale Extra*, 1999. Available at <http://www.kirj.ee/public/oilshale/Est-OS.htm>, last accessed 28.09.2011.
8. Soone, J., Doilov, S. Sustainable utilization of oil shale resources and comparison of contemporary technologies used for oil shale processing. *Oil Shale*, 2003, **20**(3S), 311–323.
9. Kõulaots, I., Goldfarb, J. L., Suuberg, E. M. Characterization of Chinese, American and Estonian oil shale semicokes and their sorptive potential. *Fuel*, 2010, **89**(11), 3300–3306.
10. Mõtlep, R., Kirsimäe, K., Talviste, P., Puura, E., Jürgenson, J. Mineral composition of Estonian oil shale semi-coke sediments. *Oil Shale*, 2007, **24**(3), 405–422.
11. Kattai, V. *Oil Shale – Source of Oil*. Tallinn, Geological Survey of Estonia, 2003. (in Estonian).
12. *List of Waste, Including Hazardous Waste. Regulation of the Government of the Republic of Estonia*. Riigi Teataja RT I 2004, 23, 155 (in Estonian). Available at <https://www.riigiteataja.ee/akt/1053350?leiaKehtiv>, last accessed 22.08.2011.
13. Arro, H., Prikk, A., Pihu, T. Reducing the environmental impact of Baltic Power Plant ash fields. *Oil Shale*. 2003, **20**(3S), 375–382.
14. Talviste, P. Geotechnical and filtration properties of oil shale ash on the basis of Kohtla-Järve Power Plant ash deposits. In: *Proceedings of XIII Estonian Geotechnical Conference* (P. Ilves, ed.). Tallinn, Estonian Geotechnical Society, 2008, 54–62 (in Estonian).
15. Taylor, J. C. Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile. *Powder Diffr.*, 1991, **6**(1), 2–9.

16. Anthony, E. J., Bulewicz, E. M., Dudek, K., Kozak, A. The long term behaviour of CFBC ash–water systems. *Waste Manage*, 2002, **22**(1), 99–111.
17. Liira, M., Kirsimäe, K., Kuusik, R., Mõtlep, R. Transformation of calcareous oil-shale circulating fluidized-bed combustion boiler ashes under wet conditions. *Fuel*, 2009, **88**(4), 712–718.
18. Myneni, S. C. B., Traina, S. J., Logan, T. J. Ettringite solubility and geochemistry of the $\text{Ca}(\text{OH})_2\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ system at 1 atm pressure and 298 K. *Chem. Geol.*, 1998, **148**(1–2), 1–19.
19. Taylor, H. F. W., Famy, C., Scrivener, K. L. Delayed ettringite formation. *Cement Concrete Res.*, 2001, **31**(5), 683–693.
20. Collepardi, M. A State-of-the-art review on delayed ettringite attack on concrete. *Cement Concrete Comp.*, 2003, **25**(4–5), 401–407.
21. Mehta, P. K. Effect of lime on hydration of pastes containing gypsum and calcium aluminates or calcium sulfoaluminate. *J. Am. Ceram. Soc.*, 1973, **56**(6), 315–319.
22. Stark, J., Bollmann, K. Delayed ettringite formation in concrete. In: *Proceedings of XVII Symposium on Nordic Concrete Research*, 1999, 4–28.
23. Chartschenko, I., Volke, K., Stark, J. Untersuchungen über den Einfluß des pH-Wertes auf die Ettringitbildung. *Wissenschaftliche Zeitschrift der Hochschule für Architektur und Bauwesen Weimar*, 1993, **39**, 171–176 (in German).
24. Pihu, T., Arro, H., Prikk, A., Rootamm, R., Konist, A., Kirsimäe, K., Liira, M., Mõtlep, R. Oil shale CFBC ash cementation properties in ash fields. *Fuel*. 2012, **93**, 172–180.
25. Arro, H., Pihu, T., Prikk, A., Rootamm, R., Konist, A. Comparison of ash from PF and CFB boilers and behaviour of ash in ash fields. In: *Proceedings of the 20th International Conference on Fluidized Bed Combustion* (G. Yue, H. Zhang, C. Zhao, Z. Luo, eds.). Springer Berlin Heidelberg, 2010, 1054–1060.

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