

PROPERTIES AND ENVIRONMENTAL IMPACT OF OIL SHALE ASH LANDFILLS

TÕNU PIHU^{(a)*}, ALAR KONIST^(a), ERIK PUURA^(b),
MARTIN LIIRA^(c), KALLE KIRSIMÄE^(c)

^(a) Department of Energy Technology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

^(b) University of Tartu, Ülikooli 18, 50090 Tartu, Estonia

^(c) Department of Geology, University of Tartu, Ravila 14A, 50411 Tartu, Estonia

Abstract. Estonia's basic power supply is covered mainly by oil shale-fired thermal power plants. The pulverized combustion (PC) and circulating fluidized bed combustion (CFBC) technologies are used. The power plant exploitation has revealed the emission of gaseous pollutants, as well as ash handling problems. The hydro ash removal is used at large power plants in Estonia. An overview of the formation and properties of oil shale ash is given. The polluting impact of ash in contact with water is analyzed. Taking into account precipitation and evaporation conditions the amount of water bound by ash as well as ash field water balance is given. The leaching behaviour of oil shale ash is analyzed. The analysis of the ash field structure shows that the degree of water penetration of the ash field body meets the requirements for hazardous waste landfills. The water permeability through dense layers ranges from 0.15×10^{-9} to 16.1×10^{-9} m/s.

Keywords: oil shale ash, landfill, leaching, environmental impact.

1. Introduction

Estonia's basic power supply is provided mainly by oil shale-fired thermal power plants. Every year 14–17 million tons of oil shale (ash content 43–57%) is fired in power plants [1]. The pulverized combustion (PC) and circulating fluidized bed combustion (CFBC) technologies are used. The properties of ash from both technologies have been thoroughly investigated [2–6]. The PC boilers were commissioned between 1959 and 1973. Due to the ageing of PC and related environmental and economic problems, the old energy units are being replaced by those employing the CFBC technology. The CFBC units ($2 \times 215 \text{ MW}_{el}$) were put into operation in 2003–2004 [7].

* Corresponding author: e-mail tonu.pihu@taltech.ee

Another, 300 MW_{el} unit was commissioned in 2018 to meet Directive 2010/75/EU on industrial emissions [8].

The use of oil shale at power plants as fuel is accompanied by a number of problems, both technical and environmental, the latter being related to the emission of gaseous pollutants, as well as ash handling. An enormous amount of alkaline ash, 7–8 million tons per annum, is left over at power plants from oil shale burning, which is deposited nearby [2]. At the same time, the ash fields and sediment ponds formed are located by the Narva River, a significant waterway that connects the fourth largest lake in Europe, Lake Peipsi, with the Gulf of Finland. Therefore, these ash waste fields which may potentially release contaminated water to the Narva River are carefully kept an eye on.

Historically, oil shale ash has been disposed of in two ash fields located at Balti and Eesti Power Plants (PP) (Fig. 1). One CFBC energy unit is in operation at the Balti PP and its ash is deposited in the Balti PP's ash field No 1. The ashes from four PC and two CFBC power units from Eesti and Auvere PPs and from three Oil Plants are deposited in the Eesti PP's ash field, making it the main solid ash waste depository.

The aim of this paper is to give an overview of the formation and properties of oil shale ash and analyze its environmental impact, groundwater included.

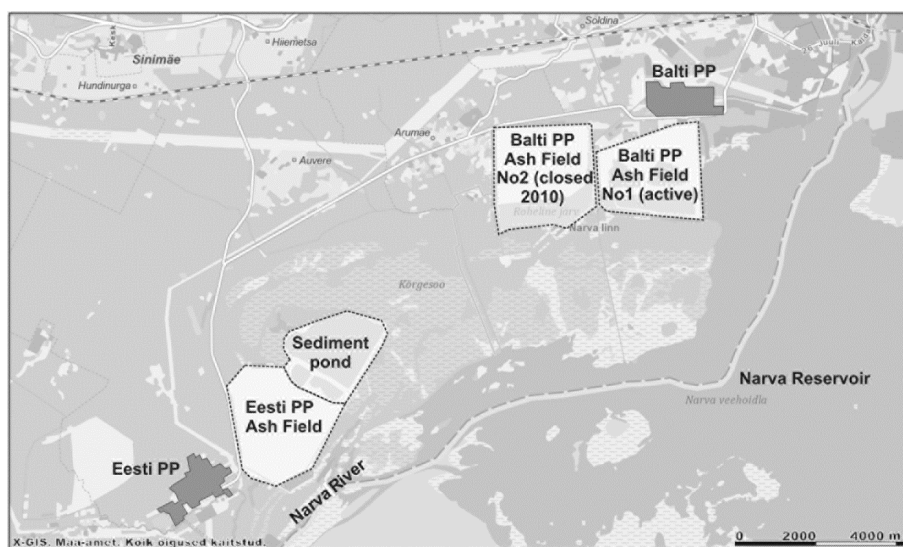


Fig. 1. Location of the Eesti Power Plant (PP), Balti Power Plant (PP) and respective ash fields and sediment ponds. (Map compiled on the Basic map of Estonia, Maaamet 2018.)

2. Composition and properties of oil shale ash

2.1. Composition of oil shale mineral part

The average mineral composition of Estonian oil shale mineral part is in detail described by Pihu et al. [9] and Kuusik et al. [10]. The mineral part of oil shale consists of two main components – carbonate and terrigenous sandy clay [7]. The recalculated content of the main minerals in the oil shale mineral part is given in Table 1. The minerals content is calculated based on the average content of carbonates and sandy-clay minerals in oil shale with a lower calorific value of 8.40 MJ/kg, which is found using the method developed by Arro et al. [11]. Calculations show the dry mineral matter of oil shale to contain 63.7% carbonates (K^d) and 36.3% sandy-clay minerals (L^d). In Table 1, minerals with contents exceeding 8% only are presented, which represent 91.3% of all minerals in oil shale.

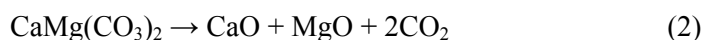
Table 1. Recalculated contents of the main mineral compounds in raw oil shale, wt%

Compound	
Calcite	44.0
Dolomite	19.5
Quartz	8.7
K-feldspar	10.5
K-mica/illite	8.6
Total	91.3

2.2. Behavior of oil shale mineral compounds during combustion

During oil shale combustion there take place three types of processes: 1) thermal decomposition of simple mineral compounds and some volatile compounds, 2) formation of new mineral compounds, and 3) changes in the mineral phase.

The decomposition of oil shale carbonate minerals during heating takes place according to the following chemical reactions:



The decomposition processes start at temperatures below 800 °C and depend on the partial pressure of CO_2 in flue gas. CaO and MgO stay in ash free oxides and CO_2 volatilizes. The decomposition of dolomite, $\text{CaMg}(\text{CO}_3)_2$, occurs in two steps: MgCO_3 decomposes at lower temperatures and CaCO_3 at higher temperatures. The extent of carbonates decomposition (ECD) k_{CO_2} is 0.97 in PF boilers, but 0.65 in CFBC boilers because of lower temperatures in the furnace. One of the most active compounds during oil shale mineral part decomposition is CaO which reacts with SiO_2 and other mineral compounds, as found by Konist et al. [12].

The silicate part of oil shale is stable at lower temperatures, except for the dehydroxylation of micas and clay minerals and the oxidation of pyrite FeS_2 , which is typically present in oil shale as a trace mineral.

A major difference between the combustion processes in PC and CFBC systems is in combustion temperature, which is about 800 °C lower in CFBC, so, only part of the carbonate component is decomposed. Most of the new mineral compounds in the ash are formed as a result of the high reactivity of calcium oxide at high temperatures, leading to its reaction with quartz and aluminosilicates, forming belite, merwinite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, akermanite/melilite and pseudowollastonite type phases, which melt at temperatures above 1100 °C. Sulphur from pyrite and organic matter is released into the gaseous phase and part of it reacts also with calcium oxide, forming anhydrite (CaSO_4).

3. Key properties of oil shale ash

The oil shale ash from power plant boilers is not considered toxic [13, 14]. If properly used, the ash can be applied for various purposes. Meeting the respective quality and safety requirements established by Estonian laws [15], oil shale ash can be used in agriculture as a fertilizer. Due to its alkalinity, the ash is also suitable to be used for reducing the acidity of soil. Moreover, in Estonia, oil shale ash has found application as a raw material in the production of cement and ash blocks for a long time already.

The chemical and mineral composition of oil shale (bituminous limestone) and its high alkalinity ash have been investigated by Loo et al. [2], Pihu et al. [9] and Kuusik et al. [10]. Laboratory scale experiments carried out by Hadi et al. [16] and Hadi and Abdelhadi [17] also demonstrated that oil shale ash was suitable for the manufacture of building materials and could be used as a soil stabilization agent in agriculture as well.

Nevertheless, the ash fields are considered environmentally hazardous because of the high content of free lime (CaO_{free}) in it. The free lime content in the PC ash is approximately 20% and that in the CFBC ash is usually up to 10% (Table 2) [13]. Coming into contact with water, free lime reacts with it, affording a water soluble $\text{Ca}(\text{OH})_2$, while at the same time, the alkalinity of water increases to $\text{pH} > 9$. The high pH of water, 12–13, makes it environmentally hazardous [14].

The properties of the ash field are greatly affected by its degree of cementation (binding ability). The cementation of ash field materials prevents water from accessing the $\text{Ca}(\text{OH})_2$ contained in them, and reduces the permeability of water.

The main streams of PC ashes come from the furnace and the cyclone, the CFBC ash is mostly bottom ash and ESP 1 field fractions.

Table 2. Chemical composition of oil shale ashes [13]

Component	Content, %					
	Bottom ash	ESP 1 field	Total ash	Bottom ash	Cyclone	Total ash
	CFBC ash			PC ash		
SiO ₂	11.26	38.58	25.06	18.90	22.07	21.77
Fe ₂ O ₃	3.12	4.86	4.01	5.28	5.12	5.17
Al ₂ O ₃	4.38	11.86	6.31	4.59	5.77	6.32
CaO	48.90	27.98	36.39	55.35	53.24	49.96
CaO (free)	13.88	8.36	9.33	26.63	22.95	21.80
MgO	6.37	4.53	5.45	7.77	7.06	6.76
K ₂ O	1.15	4.47	2.76	1.36	1.53	2.34
Na ₂ O	0.10	0.24	0.20	0.12	0.10	0.12
SO ₃ (total)	13.83	4.10	7.03	2.43	1.45	3.70
CO ₂	11.90	5.28	11.65	2.70	1.42	2.08
CO ₂ (CaO)	38.07	21.78	28.33	43.09	41.45	38.90
CO ₂ (MgO)	6.72	4.78	5.75	8.20	7.45	7.13
CO ₂ (total)	44.79	26.56	34.08	51.29	48.90	46.03
k _{CO2} *	0.734	0.801	0.658	0.947	0.971	0.95

* k_{CO2} indicates the extent of carbonates decomposition.

4. Ash handling system

In oil shale-fuelled power plants, the hydraulic ash handling system is used. The ash from CFBC and PC boilers is mixed with water at a ratio of 1:20 and the formed mix is pumped through the pipes to the ash field where settling occurs as described by Pihu et al. [9]. The system is composed of two ponds. The ash-water mixture is first pumped to the upper sediment pond where most ash particles become settled and the water flows into the lower pond for the final settling of suspended particles, and then flows back to the power plant through the collecting channels, after which the whole process recurs [9].

4.1. Ash field water balance

At present, the quantity of the circulating water (Q_{circ}) in the system is about 15–20 m³ per ton of ash. The ash itself binds ca 0.6–0.7 m³ water (Q_{bound}) per ton of ash. Thus, the quantity of water bound by ash depends on the quantity of ash stored. In addition, the water balance of the ash field is also affected by weather conditions. The average annual rainfall in northeastern Estonia is ca 600–700 mm. This means that the average annual precipitation onto the ash field of the Eesti Power Plant is about 4.7 million m³ (Table 3). Estonia is located in the temperate climate zone where the annual rainfall is usually higher than water evaporation.

Table 3. Water balance of the ash field for Eesti PP [8]

Parameter	Unit	Eesti PP
Total ash field area	10 ⁶ m ²	8.10
Ash deposit area	10 ⁶ m ²	5.00
Sediment ponds area	10 ⁶ m ²	3.10
Water in ponds	10 ⁶ m ³	1.86
Ash added to the ash field (annually)	10 ⁶ t/a	7.10*
Balance		
Water bound by ash (calc.)	10 ⁶ m ³ /a	3.59
Water evaporated	10 ⁶ m ³ /a	2.92
Technical water added	10 ⁶ m ³ /a	0.38
Precipitation onto the ash field	10 ⁶ m ³ /a	4.73
Annual water balance (approx.)	10 ⁶ m ³ /a	-1.40

* Includes ash from the Oil Plant [18].

4.2. Ash field body

The ash fields are built of hydrated ash deposited from the slurry flow. Earlier it has been shown that the ash fields have a layered structure [12]. The density, strength, and probably also the size of individual segments, may vary in fairly large limits, and there is no general distinctive trend in the mechanical and chemical properties of ash sediments. The density and strength of ash layers were found to be related to the grain size of the initial ash. Coarse grained bottom ash fractions form loose and gravelly ash layers that are easy to break whereas fine grained ash with the best binding properties forms almost impermeable hard layers. As a result, the conductivity of water in hard layers can be as low as 0.15×10^{-9} – 16.1×10^{-9} m/s. These hard and impervious horizontal layers ensure that the rainwater or sediment ponds water will not easily infiltrate into the sediment pile but will flow on the slopes and be collected in back-flow channels. Irrespective of the location and depth of the sediment pond it is to be considered that ash sediments contain portlandite [Ca(OH)₂] and ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O], which indicates that virtually the entire ash field material contains strong alkali compounds. The leaching tests carried out by Arro et al. [13] on sediment samples showed the ash field material to contain up to 2% of the water-soluble substance. The solid leach product from the aqueous solution is highly alkaline, with pH exceeding 12.

5. Leaching behaviour of Estonian oil shale ash

The leaching behavior of Estonian oil shale ash is dependent on its mineral and chemical composition. The mineral composition depends on the burning technology used as the temperature ranges from 800 °C in the CFBC boiler to nearly 1400 °C in the PC boiler. The mineral composition of different ash

fractions from PC and CFBC systems are discussed in detail by Pihu et al. [9], Bityukova et al. [19] and Liira et al. [20].

Although calcium oxide is highly reactive towards other minerals and gases at high temperatures, the residence time during which the combustion takes place is not sufficient for the reactions to be completed and a significant part of calcium oxide remains in the ash in free form. Liira et al. [20] detected that free MgO (periclase) was also present in the ash, but its reactivity towards water was significantly lower than that of free CaO. Thus, free CaO has the main role in the reactions of ash with water. Due to the exothermicity the reaction of free CaO with water generates heat. In the mixture of free CaO and water, the pH of the solution is determined by the solubility of portlandite, Ca(OH)_2 . However, the solubility of free CaO is also temperature dependent. At hydrochemical equilibrium in the portlandite-water system, the pH is 12.4 at 25 °C and 13.6 at 0 °C. The hydration reaction is fast since the hydrochemical equilibrium is reached within minutes.

Of the other minerals in the Ca(OH)_2 -dominated system, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and anhydrite are actively participating in the reactions with water and Ca(OH)_2 during several days or weeks. The role of belite, K-feldspar, K-mica/clay minerals and the glass phase in the formation of new minerals and in changing the chemical composition of the pore water becomes evident after months or years [21].

5.1. The change in pH during the reaction of dry ash with water

Whether or not water is used for ash transport, in Estonian climatic conditions, the ash reacts with water and air moisture. When dry ash comes into contact with excess water, the reaction time during which the aqueous solution becomes strongly alkaline is seconds or minutes, depending on the solid/liquid ratio.

Figure 2 shows the change in the pH of PC and CFBC ashes with time at different solid/liquid (S/L) ratios. The tests were carried out for 10 minutes while the solution temperature was increased from 9 to 14 °C at an S/L ratio of 1:5. At lower S/L ratios, the temperature increase recorded was smaller. The experiment showed that already after 10 minutes, the PC ash-water mixtures had pH > 10 at an S/L ratio of 1:4000, pH > 11 at an S/L ratio of 1:2000 and pH > 12 at an S/L ratio of 1:200. When the S/L ratio was 1:25, the pH exceeded 12.5. The leaching modes of PC and CFBC ashes were different. With the CFBC ash the pH > 10 was achieved at an S/L ratio of 1:1500, pH > 11 at an S/L ratio of 1:1000 and pH > 12 at an S/L ratio of 1:100. This is explained by the lower free CaO content in the CFBC ash. Therefore, the increase of pH may be accounted for by a simple reaction of free CaO with water during its hydration.

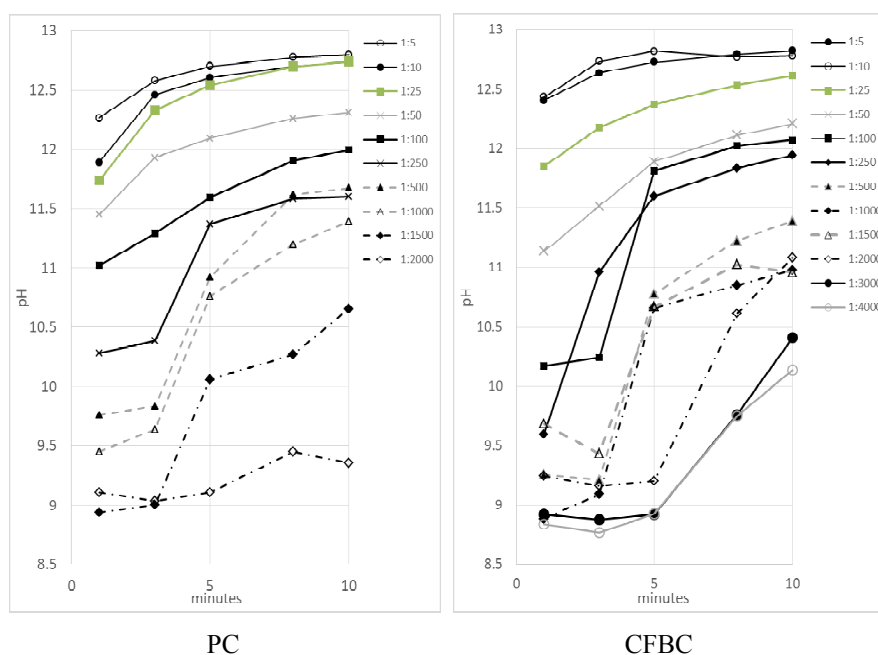


Fig. 2. Change in pH in time for different solid/liquid ratios for PC and CFBC ashes.

5.2. Long-term chemical reactions

After the first active period of reaction of free CaO with water, in a few days all free CaO is hydrated and the compound solution is dominated by the solubility and precipitate of portlandite. The other important reaction that occurs during the first two weeks or months is the formation of ettringite [20]. The formation of ettringite favours the crystallization of ash sediments and contributes to the consumption of pore water. The limiting factor in ettringite formation, in the presence of excess water, is the existing amount of CaSO_4 . The ettringite formation depends also on the availability of water. The formation of ettringite is stopped until a sufficient amount of water is available. If the ash is disposed of in a way that there is no water available for ettringite formation, then the crystallization occurs at a later stage with the help of infiltrating groundwater. The crystallization energy of ettringite is higher than that in its delayed formation, and after water becomes available, the swelling and formation of cracks may occur in the ash plateau. Therefore, right after the ash disposal to the field during the first two months there must be excess water present for ettringite formation to guarantee the stability and low hydraulic conductivity of water in the ash plateau.

There occur a series of chemical reactions in the ash plateau in the long term – for months and even years after ash disposal. Of these reactions, the crystallization of the K-containing glass phase and the reaction between $\text{Ca}(\text{OH})_2$ and other K-containing minerals (K-feldspar, clay minerals) are the

most significant. The products of those reactions are new Ca-silicates and Ca-alumosilicates and their hydrates. During that period Ca^{2+} is removed from the pore water and is replaced by K^+ . Therefore, the water that is leached out from the ash plateaus in the longer term is poorer in Ca, at the same time, it has high concentrations of K-ions. Also, belite is hydrated during the reactions occurring for months or years.

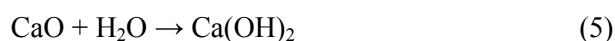
5.3. Reactions between ash and surrounding atmospheric CO_2

Another important topic to consider is the reactions between the mineral compounds of ash and atmospheric CO_2 . These reactions have a double positive effect on the environment: they consume atmospheric CO_2 and transform alkaline mineral compounds into carbonates, decreasing thereby the possibility of alkaline leaching.

Under atmospheric conditions, the transformation of free CaO into CaCO_3 is carried out through the water phase only:



Between these two reactions there takes place an intermediate process of $\text{Ca}(\text{OH})_2$ accumulation:



At the same time, the dissolution and carbonation of ettringite will lead to the removal of CO_2 .

In addition, it should be noted that CO_2 is removed also by the dissolution of calcium hydroxide and mixing of Ca-rich alkaline water with groundwater:



Therefore, the content of free lime (CaO) in dry ash, which is 78.6 wt%, determines the potential of ash for removal of CO_2 from the atmosphere. As long as portlandite $\text{Ca}(\text{OH})_2$ and ettringite are present in the ash, its potential for removal of CO_2 is not fully realized.

5.4. The composition of water circulating in the hydraulic ash removal system

In the ash hydro-transport system and sediment ponds, the composition of water depends on the mineral composition of ash and the chemical reactions determined by minerals solubility, temperature, reaction kinetics, access of atmospheric CO_2 and operation dynamics of the system, including seasonal variations. Earlier it has been shown that the composition of water originating from the ash field does not depend so much on the solubility of minerals

at that particular location but on the transport of water to the location as well as on the reactions having occurred along the flow path [22]. The initial composition of water after its first contact with ash is prevailed by Ca^{2+} , OH^- and SO_4^{2-} ions as a result of free lime hydration and anhydrite dissolution, accounting for 80–95% of the total dissolved ions and complexes (Table 4) [9]. The alkalinity of the ash field water is more than 50 mg-eq/l, but may increase up to 60–70 mg-eq/l. When this highly alkaline water comes into contact with the surrounding atmosphere, it will react with the atmospheric CO_2 , which results in the precipitation of CaCO_3 .

Table 4. Chemical composition (mg/l) and pH of the sediment pondwater (data from [9])

Component	Value
pH	12.2–13
Na^+	100–180
K^+	3000–4765
Ca^{2+}	400–800
NH_4^+	0–1
Cl^-	720–1070
SO_4^{2-}	1043–2960
OH^-	1037–1395
CO_3^{2-}	1–360

The variations of the pH of the sediment pond water are mostly due to temperature changes and partly due to the precipitation of atmospheric fresh-water. The K/Ca ratio expresses the dominance of long-term reactions over the dissolution reactions of fresh ash, whereas the presence of the CO_3^{2-} ion shows that the system is open to the atmosphere and there (e.g. in sediment ponds) takes place the removal of CaCO_3 . The variation in SO_4^{2-} ion content depends on the solubility of gypsum and ettringite and behaves opposite to that in Ca^{2+} content.

In sediment ponds, the carbonization of calcium and hydroxide rich water occurs by diffusion of CO_2 from air into the water. In the surface layer of the sediment pond, there is formed colloidal CaCO_3 , which is further converted into CaCO_3 crystals that precipitate on the sediment pond bottom. In addition, as a result of temperature changes at the bottom of sediment ponds, the precipitation of Ca(OH)_2 occurs because in warm climate conditions the solubility of Ca(OH)_2 is lower, while in winter with water freezing the oversaturation of Ca(OH)_2 takes place. This suggests that there are competing mechanisms of precipitation of calcium hydroxide and calcium carbonate, depending on climatic conditions.

5.5. Concentration and geochemical behavior of trace metals

The concentration of trace metals in the oil shale ash from Estonian power plants is low. This is related to the depositional setting of kukersite oil shale,

which is dominated by normal marine carbonate rocks where heavy metals did not accumulate. During combustion when different ash fractions are removed, its trace element concentrations increase. However, several studies have shown the content of trace metals in dry ash to be below the limit values set for residential regions [23–25]. The only exception is arsenic in the ash, which comes from electrostatic precipitators (40 mg/kg compared to the limit value of 20–30 mg/kg for residential areas and 50 mg/kg for industrial zones). Still, the amount of ash originating from electrostatic precipitators amounts to only 23 wt% of the total ash generated in the boilers. At the same time, the concentration of As in the ash from the other parts of the boiler is 11–14 mg/kg. It is evident that the concentrations of none of the trace metals in the overall dry ash exceed the limits set for soil even for residential areas.

Another question is whether alkaline conditions mobilize any of the trace metals at hazardous concentrations. The batch leaching experiments on ashes at a liquid-to-solid ratio of 10 for materials with a particle size below 4 mm [26] showed that only the leachability of selenium (Se) of the ash from electrostatic precipitators was 0.82 mg/kg, which is higher than the limit value for the waste to be characterized as non-hazardous (0.5 mg/kg), but much lower for the waste to be characterized as hazardous (7 mg/kg). Moreover, the leachability of Se in the other fractions of ash was determined to be in the range of 0.03–0.18, which is well below the limit allowing the ash to be defined as non-hazardous waste. Although the pH of the leachate in our tests was as high as 12.9, the leachability studies of trace metals carried out by us revealed that ash could be defined as non-hazardous.

6. Conclusions

The use of oil shale for power generation is unique not only in the European Union, but throughout the world. Estonian power plants operating on oil shale use water for the removal and stabilization of ash products. Therefore, the best practices for the ash disposal in ponds are imperative. There is a clear need to better understand the leaching behaviour and environmental impact of the ash disposed of in ponds.

The water used for ash removal and stabilization circulates in a closed loop system. However, the water balance of the ash landfilled in the Eesti Power Plant's sediment ponds demonstrates that due to the simultaneous operation of a number of power units and the lateral ash field area, as well as climatic precipitation and evaporation rates characteristic of Estonian climate cause a permanently high demand for fresh water. The formation of hard impermeable ash layers with a permeability as low as 0.15×10^{-9} to 16.1×10^{-9} m/s ensures that the prevailing part of the rainwater and snow-melt will be removed as the surface run-off. In this sense water penetration rates in the layered structure of the ash deposit formed by employing the

current ash handling technology fulfils the requirements for clay barriers used in hazardous waste landfills.

In dry state, the oil shale ash contains a significant amount of free lime, more than 10%. When coming in contact with water, free lime starts to react with it within seconds or minutes, causing the pH of the solution to exceed 12 at a liquid/solid ratio of 200 or lower for the PC ash and at a liquid/solid ratio of 100 or lower for the CFBC ash. After sedimentation, carbon dioxide from the atmosphere is consumed and held in the atmosphere/wet ash and atmosphere/alkaline water interfaces, i.e. the upper layers of the ash plateau and the surface layer of the secondary sediment pond, which decreases the amount of leachable alkaline minerals in the ash. In the long term, the chemical reactions taking place in the plateau lead to the replacement of Ca^{2+} by K^+ in the circulating water.

The only major problem related to the leaching of ash into water is the alkalinity of the latter caused by the hydration of CaO, dissolution of portlandite and replacement of Ca^{2+} by K^+ . As the trace metals concentration in kukersite is low, it is low also in dry oil shale ash and the leachate. The concentration of trace metals in dry ash is lower than the limits set for soils in residential areas. Similarly, the concentration of trace metals in the leachate (batch experiments at a liquid/solid ratio of 10) is lower than the limits set for non-hazardous waste. Thus, there is no evidence of ground-water pollution which could potentially impose risks to human health.

REFERENCES

1. Konist, A., Maaten, B., Loo, L., Neshumayev, D., Pihu, T. Mineral sequestration of CO_2 by carbonation of Ca-rich oil shale ash in natural conditions. *Oil Shale*, 2016, **33**(3), 248–259.
2. Loo, L., Maaten, B., Konist, A., Siirde, A., Neshumayev, D., Pihu, T. Carbon dioxide emission factors for oxy-fuel CFBC and aqueous carbonation of the Ca-rich oil shale ash. *Energy Procedia*, 2017, **128**, 144–149.
3. Pihu, T., Konist, A., Neshumayev, D., Loo, L., Molodtsov, A., Valtsev, A. Full-scale tests on the co-firing of peat and oil shale in an oil shale fired circulating fluidized bed boiler. *Oil Shale*, 2017, **34**(3), 250–262.
4. Konist, A., Valtsev, A., Loo, L., Pihu, T., Liira, M., Kirsimäe, K. Influence of oxy-fuel combustion of Ca-rich oil shale fuel on carbonate stability and ash composition. *Fuel*, 2015, **139**, 671–677.
5. Konist, A., Pihu, T., Neshumayev, D., Külaots, I. Low-grade fuel – oil shale and biomass co-combustion in CFB boiler. *Oil Shale*, 2013, **30**(2S), 294–304.
6. Konist, A., Pihu, T., Neshumayev, D., Siirde, A. Oil shale pulverized firing: boiler efficiency, ash balance and flue gas composition. *Oil Shale*, 2013, **30**(1), 6–18.
7. Ots, A. *Oil Shale Fuel Combustion*. Tallinna Raamatutrükikoda, Tallinn, 2006.
8. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions (integrated pollution prevention and control). <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32010L0075>

9. 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.
10. Kuusik, R., Uibu, M., Kirsimäe, K., Mõtlep, R., Meriste, T. Open-air deposition of Estonian oil shale ash: formation, state of art, problems and prospects for the abatement of environmental impact. *Oil Shale*, 2012, **29**(4), 376–403.
11. Arro, H., Prikk, A., Pihu, T. Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products. Part 1. Calculation on the basis of heating value. *Fuel*, 2003, **82**(18), 2179–2195.
12. Konist, A., Pihu, T. Reducing CO₂ emissions with oil shale circulating fluidized bed boiler ash. In: *Proc. of the 21st Int. Conf. on Fluidized Bed Combustion*, 2 (Editore, E. A., ed.). The 21st International Conference on Fluidized Bed Combustion, 3rd–6th June 2012, Naples, Italy.
13. Arro, H., Pihu, T., Prikk, A., Rootamm, R., Konist, A. Comparison of ash from PF and CFB boilers and behavior of ash in ash fields. In: *Proc. of the 20th Int. Conf. on Fluidized Bed Combustion. II* (Yue, G., Zhang, H., Zhao, C., Luo, Z., eds.). China, Xi'an, May 18–21, 2009. China, Tsinghua University Press/Springer, 1054–1060.
14. Arro, H., Prikk, A., Pihu, T. Reducing the environmental impact of Baltic Power Plant ash fields. *Oil Shale*, 2003, **20**(3S), 375–382.
15. *Certificate of Conformity CS No. 003697 of Estonian Plant Production Inspectorate*, 11.09.2000 (in Estonian).
16. Hadi, N. A., Khoury, H. N., Suliman, M. S. Utilization of bituminous limestone ash from El-Lajjun area for engineering applications. *Acta Geotech.*, 2008, **3**(2), 139–151.
17. Hadi, N. A. R. A., Abdelhadi, M. Characterization and utilization of oil shale ash mixed with granitic and marble wastes to produce lightweight bricks. *Oil Shale*, 2018, **35**(1), 56–69.
18. Eesti Energia. *Annual Report 2017. Environmental Report*. https://www.energia.ee/-/doc/8457332/ettevottest/investorile/pdf/annual_report_2017_eng.pdf (retrieved on 06.11.2018).
19. Bityukova, 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.
20. 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.
21. 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.
22. *Ash Materials and Ash Fields* (Melentjeva, V., ed.). Energiya, Moscow, 1978, 296 pp (in Russian).
23. Laja, M. *Oil Shale Ash, Properties and Behaviour in Water Medium*. Master Thesis, University of Tartu, 2005 (in Estonian).
24. Kahru, A., Sihtmäe, M. *The Influence of the Eco-Toxicity of Product while Neutralizing – Carbonizing Oil Shale Ash by CO₂*. Research report, part 3. National Institute of Chemical Physics and Biophysics, Tallinn, 2007 (in Estonian).

25. *Evaluation of Environmental Influence of Closure of Balti Power Plant's Ash Field No. 2*. Report. AS Maves, LHK, AS PIC Eesti, AS Merin. Tallinn, 2002 (in Estonian).
26. European Standard EN 12457-2. *Characterization of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 2*. European Committee for Standardization Brussels, 2003.

Received December 12, 2018