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Quantification of oil shale industry ash flows – their chemical and mineralogical composition

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Abstract. *The global demand for resources is escalating in today's rapidly evolving world. As traditional raw materials become scarcer and more expensive, alternative sources have to be found. One such emerging resource is oil shale ash. This article provides a comprehensive overview of the various fractions of oil shale ash generated in the oil shale industry in Estonia. The ash results from the direct combustion of oil shale with pulverised combustion (PC) and circulating fluidised bed combustion (CFBC) technologies, as well as from shale oil production processes. It offers detailed information about the proportions of ash derived from different technological processes and a thorough analysis of their mineralogical and chemical compositions, trace element content, and leaching characteristics. By examining these diverse characteristics, the study enhances understanding of the ash's potential implications and applications.*

Keywords: *oil shale ash, ash characterisation, material recovery, leaching.*

1. Introduction

The United Nations Environment Programme's Global Resources Outlook reported that in 2019, the global economy consumed a total of 105.7 billion tonnes of materials [1]. Of this, roughly 91% was sourced through direct harvesting and extraction, while only 9% came from recycled and recovered resources. Global demand for natural resources is steadily rising, with projections indicating a 60% increase in resource consumption by 2060 compared to 2020 levels. This rise follows a more than threefold growth in material use over the past 50 years.

The world energy sector has a substantial demand for global resources, consuming around 500 EJ of fossil fuels annually from coal, oil, and natural

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gas, with biomass contributing an additional 60 EJ, primarily for heat and power [2]. While these fuels require large resource inputs, their combustion produces significant amounts of ash that can be repurposed. This ash, which comes from a range of sources, including biomass, municipal waste, coal, lignite, and oil shale, is increasingly recognised as a valuable secondary raw material. It can be used in construction materials or as a source for extracting valuable elements, reducing the need for virgin materials [3–13]. This approach helps mitigate waste and promotes a circular economy by transforming by-products into sustainable resources.

Oil shale is a type of sedimentary rock that contains a mixture of organic and inorganic matter. The organic matter of Estonian oil shale, known as kukersite, has a high hydrogen and oxygen content, low nitrogen content, and significant amounts of organic sulphur and chlorine [14, 15]. Estonia possesses substantial oil shale resources, estimated at 6.3 billion tonnes, which includes 2 billion tonnes deemed economically viable for mining. This positions Estonia among the top ten countries with the largest oil shale reserve [16]. Oil shale is used to produce energy and shale oil. Historically, Estonia was the only country operating oil shale fired power plants to supply most of its electricity, with excess power exported to neighbouring countries. However, the share of oil shale in electricity production has decreased in recent years [14]. In 2016, oil shale accounted for 80% of Estonia's electricity production; by 2023, this share had decreased to 35%, generating 7.1 TJ, as the country increased its reliance on renewable energy sources [17].

Estonia's oil shale industry (power plants and shale oil production plants) generates around 5 million tonnes of oil shale ash annually, classified in waste statistics [18] as fly ash and bottom ash. However, this classification simplifies a more complex reality. The ash can be divided into distinct fractions depending on the technology used and the specific collection points, with each fraction exhibiting unique characteristics.

In Estonia, oil shale fired power plants employ two combustion technologies: pulverised combustion (PC) and circulating fluidised bed combustion (CFBC). PC technology is used at Eesti Power Plant (Eesti PP), where the TP-101 high-pressure boilers are equipped with sulphur-capturing units. CFBC technology is employed in unit 8 of Eesti PP, unit 11 of Balti Power Plant (Balti PP), and Auvere Power Plant (Auvere PP).

In addition to power plants, Estonia also has oil shale thermal processing plants for shale oil production. There are two methods for shale oil production: gaseous heat carrier (GHC) and solid heat carrier (SHC). Utilising the SHC method, the semi-coke is combusted in a lift pipe combustor (also known as an aero-fountain combustor) or a CFB furnace, producing oil shale ash. In contrast, with the GHC method, the semi-coke is deposited in landfills [19]. Conventional SHC oil shale retorting technologies use lift pipe combustors (Enefit140 and Petroter), while Enefit280 employs CFBC technology.

Over the past two decades, there have been notable changes in the oil shale industry. Significant developments include the restructuring of power generation facilities, which involved the partial decommissioning of older PC units and the retrofitting some with new CFB boilers (at Balti PP and Eesti PP units 11 and 8, respectively, in 2004–2005). A new 305 MW$_{el}$ power unit at Auvere PP was commissioned in 2016. Some older PC units (units 3, 4, 5, and 6 at Eesti PP) were upgraded with desulphurisation (deSOx) and denitrification (deNOx) technologies between 2010 and 2012 to comply with emissions regulations [20]. Additionally, there has been a shift from using oil shale for power generation to producing shale oil, with new shale oil production plants constructed between 2009 and 2015. Furthermore, one plant is currently under construction and is planned to be operational in 2025. A summary of the current state of oil shale utilisation in power generation and shale oil production is provided in Table 1.

Table 1. Overview of the primary oil shale utilising plants (adapted from [20])

Plant	Type	Fuel	Rated capacity (gross), MW$_{el}$	Commissioning
Power plants				
Balti PP unit 11	2 CFB boilers per single turbine	Oil shale, up to 50% biomass	215 MW$_{el}$	Turbine 1970s, boilers 2005
Eesti PP unit 8	2 CFB boilers per single turbine	Oil shale, up to 50% retort gas (in one boiler)	215 MW$_{el}$	Turbine 1970s, boilers 2005
Auvere PP	1 CFB – 1 turbine	Oil shale, retort gas, up to 50% biomass	305 MW$_{el}$	2016–2018
Eesti PP units 3, 4, 5, 6	2 PC boilers per 1 turbine	Oil shale, retort gas	185–195 MW$_{el}$	1970s, deSOx 2010–2012, deNOx
Eesti PP units 1, 2, 7	2 PC boilers per 1 turbine	Oil shale	185–195 MW$_{el}$	Decommissioned 2020
Shale oil production plants				
Enefit140	SHC	Oil shale		1980
Enefit280	SHC + CFBC	Oil shale		2012
Petroter I	SHC	Oil shale		2009
Petroter II	SHC	Oil shale		2014
Petroter III	SHC	Oil shale		2015

The oil shale is pre-treated to ensure that its particle size remains within the specifications required by the combustion technology. PC technology needs pulverised oil shale with an average grain size of less than 0.01 mm. CFBC boilers use oil shale with an average grain size of up to 25 mm, although for Auvere PP, the corresponding value is approximately 10 mm, and for the Enefit280 oil plant, less than 6 mm [21].

PC technology operates at high temperatures of 1350–1450 °C (up to 1500 °C), facilitating extensive decomposition of carbonate minerals and melting of clay minerals, which leads to the formation of secondary Ca-silicate and Ca-Al-silicate phases. Conversely, CFBC technology, with its optimum furnace temperature of about 800 °C, results in only partial decomposition of calcite ($CaCO_3$) and preservation of clay mineral phases, with the loss of physically and chemically bound water. As a result, the formation of new mineral phases is less likely compared to processes operating at higher temperatures. Consequently, PC ashes are enriched in free CaO and secondary Ca-silicate phases. It should be noted that the distinction between total CaO and free CaO in different ashes is affected by the presence of indissoluble minerals, as well as variations in carbonate content. In contrast, CFBC ashes contain a higher proportion of residual mineral phases and are characterised by higher sulphur concentrations, primarily in the form of anhydrite ($CaSO_4$). This sulphur concentration is due to the nearly complete desulphurisation of flue gas, facilitated by the prolonged contact between ash particles containing $CaO/CaCO_3$ and SO_2 in flue gas, the lower temperature in the combustion chamber, and the CFBC technology process system [22, 23]

Arro et al. [24] noted significant morphological differences between CFBC and PC ashes based on surface observations. The ash particles from CFB boilers have irregular shapes, with an insignificant presence of melted spherical particles. In contrast, PC ash predominantly consists of spherical, melted particles. This difference indicates that mineral decomposition and the formation of new minerals occur at a considerably higher rate in PC boilers, where furnace temperatures exceed 1400 °C, compared to CFB boilers, which operate at around 800 °C. Additionally, the specific surface area of CFBC ashes is up to ten times greater than that of PC ashes.

Ash can be collected from the boiler unit assemblies and flue gas cleaning equipment (Fig. 1). Ash that accumulates at the bottom of the furnace is referred to as bottom ash, while the ash transported by the gas flow from the boiler is known as fly ash. Fly ash consists of particles that gravitationally settle out of the gas stream.

Depending on the technology, the ash collection points are different. For example, in a PC unit, the ash discharge points include the bottom of the furnace, external heat exchanger, superheater, economiser, air preheater, cyclone, and fabric filter. In a CFBC unit, the fly ash is precipitated in the superheater, economiser, air preheater, and electrostatic precipitators (ESP). In addition to the ESPs, Auvere PP has an extra cleaning stage using fabric filters to achieve particulate matter concentrations below 10 mg/m^3.

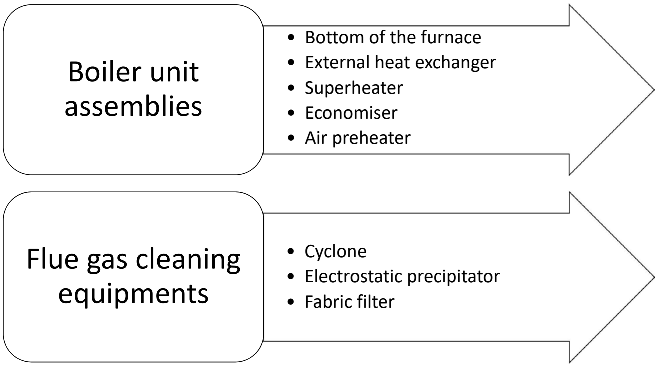

Fig. 1. Simplified scheme for possible ash collection points.

Over the years, the properties and characteristics of oil shale ash have been extensively investigated and documented [11–13, 22, 23, 25–29]. However, a comprehensive understanding of all oil shale ash fractions generated through different technologies is still lacking. As resource demand rises, maximising the efficiency of already excavated and processed materials becomes critical. Oil shale ash has considerable potential as a construction material or as a source for extracting various substances and elements. A detailed characterisation of each ash fraction is essential to fully harness this potential, enabling optimised utilisation of the material and minimising waste. Therefore, this article aims to provide a detailed overview of the properties of different types of ash from the Estonian oil shale industry, which are crucial for their effective utilisation and valorisation.

2. Materials and methods

Ash samples were collected from the operating power plants (Eesti PP, Auvere PP) and shale oil production installations (Enefit280 and Petroter). The samples were gathered over an extended period, allowing to account for potential variations in fuel composition and operational conditions. The values presented in this study represent the average composition of the fractions, providing a more representative assessment of the ash characteristics. The specific locations of ash collection are detailed in the following sections of the article.

The mineralogical composition was analysed in the Department of Geology at the University of Tartu laboratory using powder X-ray diffraction (XRD) on a Bruker D8 diffractometer equipped with SolX and super-speed LynxEye detectors. The chemical composition was determined in the laboratory of the Department of Energy Technology at Tallinn University of Technology using a Rigaku ZSX Primus II 4 kW wavelength dispersive X-ray fluorescence spectroscope (WD-XRF).

The determination of free CaO was conducted by first grinding and sieving the sample through a 100 µm mesh sieve, except in the case of fly ash, which did not require grinding. The prepared sample was then slaked with boiling water to initiate the hydration process. To enhance the solubility of calcium hydroxide, a sugar solution was introduced. The resulting solution was subsequently titrated with standardised 0.1 M hydrochloric acid, utilising phenolphthalein as an indicator to determine the endpoint. The volume of acid consumed during titration was used to quantify the free CaO content in the sample.

The mineral CO_2 content in a sample was determined by measuring the total inorganic carbon (TIC) using a Vario MACRO elemental analyser. The TIC value was then used to calculate the carbonate-derived CO_2 content.

A composite fly ash sample was employed in the leaching tests rather than utilising individual ash fractions. This composite sample was created by mixing the various ash fractions obtained from each installation. The proportions used in this mixing process were determined based on each installation's specific ash balance. This approach ensured that the composite fly ash sample accurately represented the overall ash characteristics for each installation, facilitating a more comprehensive analysis of leaching behaviour.

Leaching tests were conducted in accordance with standard EVS-EN 12457-4 [30], maintaining a liquid-to-solid ratio of 10:1. Quantification of trace elements in both ash and eluates was conducted using inductively coupled plasma mass spectrometry (ICP-MS) with a Thermo iCAP Qc, following the standard test method ASTM D6357-21a [31]. The content of sulphates (SO_4^{2-} ions) and chloride (Cl^- ions) was determined using liquid ion chromatography (IC) with a Dionex ICS-1000, in accordance with the EVS-EN ISO 10304-1:2009 standard [32].

3. Results and discussion

3.1. Auvere Power Plant

Auvere PP, completed in 2015 with acceptance tests finalised in 2018, stands as the most modern oil shale power plant in Estonia. It has a gross capacity of 305 MW_{el} and operates as a monobloc system, where a single boiler supplies steam to the turbine [33, 34]. The primary fuel is oil shale with a calorific value of 7–11 MJ/kg and a grain size of up to 10 mm. Per Auvere PP's environmental permit [35], biomass and retort gas are also co-combusted with oil shale.

Acceptance tests indicate that the net efficiency of the unit at nominal capacity and under steady-state conditions, with oil shale at a calorific value of 8.3 MJ/kg, exceeds 40%, while the boiler's efficiency surpasses 90%. The boiler operates at a temperature of around 850 °C, which significantly

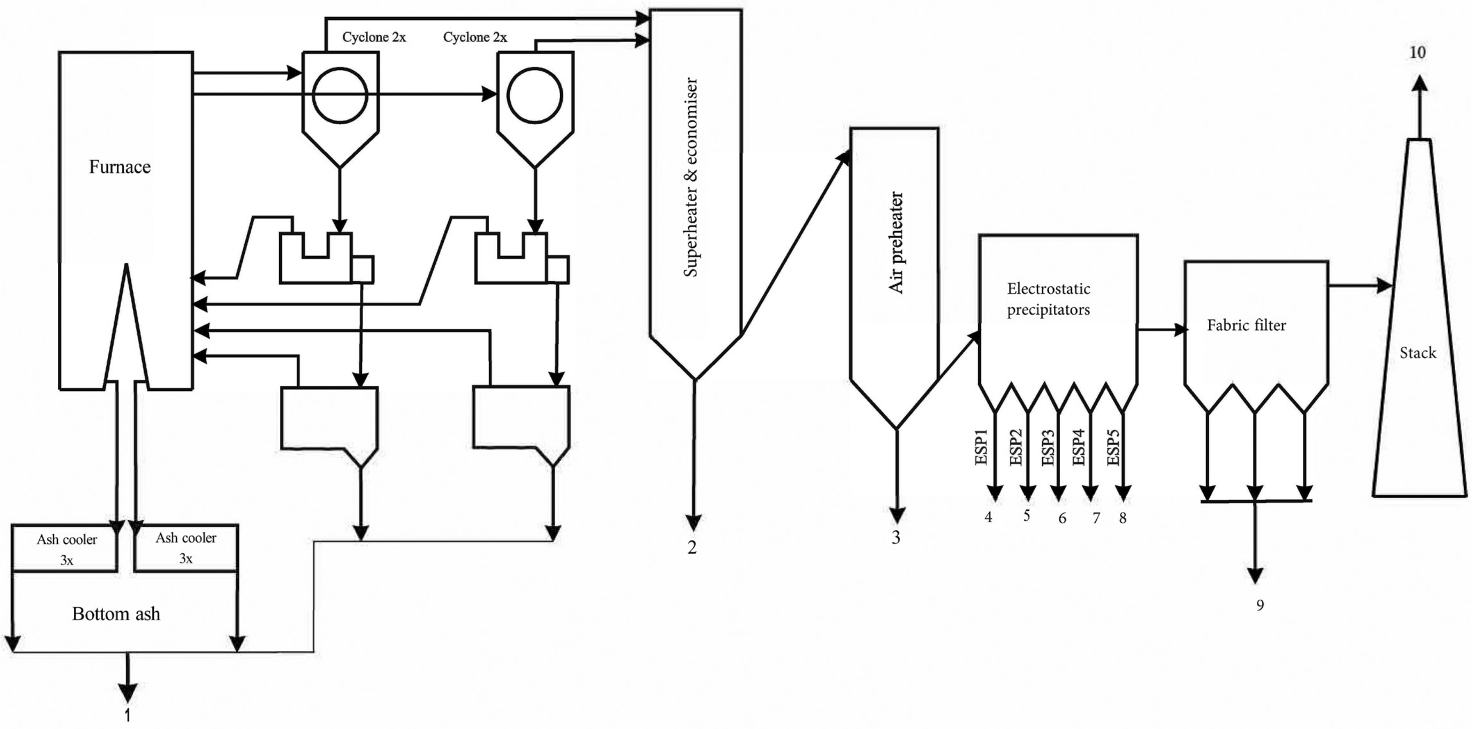

Fig. 2. Layout of Auvere Power Plant and the ash collection points (adapted from [34]): bottom ash (1), superheater and economiser ash (2), air preheater (3), electrostatic precipitators – ESP1 (4), ESP2 (5), ESP3 (6), ESP4 (7), ESP5 (8), fabric filter (9), ash in flue gas (10).

influences the decomposition behaviour of the carbonate minerals in the oil shale's mineral part. The plant layout and the main ash generation points are illustrated in Figure 2.

The annual amount of ash generated depends on the plant's capacity, plant availability, and the fuels used, and is a direct result of consumption and the open electricity market. The estimated average ash flow is 1.4 to 1.5 million tonnes per year, of which approximately 30% is estimated to be bottom ash and 70% fly ash. The ash balance of Auvere PP has not been determined experimentally. Thus, the amount of bottom ash was determined by the thermal mass balance of the bottom ash coolers. The rest of the relative ash balance of Auvere PP (Fig. 3) is based on Balti PP CFBC unit that was determined experimentally [36]. The largest share of fly ash (collection points 2 to 10) is separated from the first field of the ESP (about 50% of the total ash flow). The remaining part of the total ash flow is less than 20%, and it is estimated that most of it comes from the superheater-economiser cyclone ash (approx. 9%) and the second field of the ESP (approx. 7%). The ash fraction in flue gas (ash particles leaving the stack) is very low, and the maximum concentration allowed under the current industrial emissions legislation [37] is 10 mg/Nm^3.

The chemical composition of the ash precipitated at different points along the boiler's gas passage varies significantly. Samples from Auvere PP reveal distinct differences among ash fractions: bottom ash shows notably higher Ca and lower Si content compared to other fractions (Table 2). These observations align with findings from Ots [21] regarding CFBC ashes. However, while Ots noted that free CaO content is typically highest in the bottom ash and lowest in

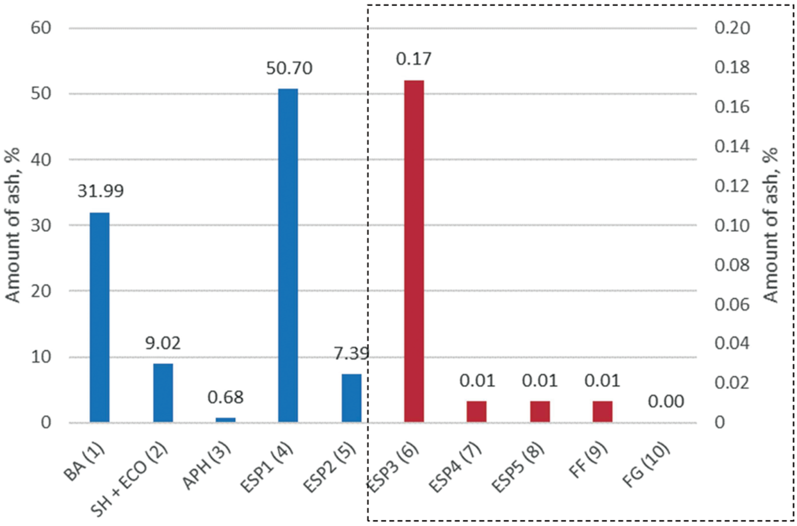

Fig. 3. Ash balance of Auvere Power Plant. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash, FG – ash in flue gas.

the finest fractions, Auvere PP's ash exhibits a slightly different pattern. Due to the finer fuel (<10 mm), combustion is more complete and uniform, leading to finer fly ash particles, which could result in the higher free CaO content in the ash collected from the final stages of the flue gas cleaning system.

Table 2. Chemical composition of the ashes from Auvere Power Plant, wt%

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
SiO_2	8.9	31.1	26.6	30.4	28.8	28.6	24.6	21.2	11.0
Fe_2O_3	2.4	3.6	3.3	3.7	3.6	3.7	3.4	2.9	8.4
Al_2O_3	1.4	6.9	5.7	6.5	6.5	6.9	6.1	5.1	2.1
CaO	52.2	36.8	39.7	37.0	39.6	37.6	41.9	46.0	47.1
MgO	5.6	5.3	5.7	4.7	5.0	4.7	4.5	4.3	2.1
Na_2O	0.05	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3
K_2O	0.6	3.5	2.7	3.6	3.4	3.5	2.8	2.3	0.7
$SO_{3(total)}$	8.0	5.9	9.6	6.5	6.4	6.5	7.6	7.0	1.9
Cl	0.2	0.5	0.5	0.6	0.5	0.5	0.7	0.7	0.4
CaO_{free}	16.7	16.1	18.2	19.0	19.3	14.2	14.4	16.2	12.8
CO_2	22.3	7.2	6.8	5.4	5.2	6.1	6.4	5.7	9.6
TIC	6.1	4.7	2.0	1.5	1.4	1.7	1.7	1.6	2.6

Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

The mineral composition supports the findings of different authors on CFBC ashes [21–23, 36], showing that calcite makes up more than 35% of the bottom ash, while in other fractions, it ranges from 9% up to 15% (Table 3). As reported by other authors [23, 24], the anhydrite content is generally high in all fractions, but slightly elevated in the bottom ash and APH ash. Longer residence time in the boiler and higher SO_2 concentrations allow better SO_2-CaO interaction, leading to higher anhydrite content compared to finer fly ash fractions. The compounds C_2S (Ca_2SiO_4) and C_4AF ($Ca_2(Al,Fe^{3+})_2O_5$), both standard components of Portland cement [38], are present in significant amounts, particularly in the ESP ash. In finer fly ash fractions, due to higher cooling rates and lower SO_2 contact, free CaO instead reacts with SiO_2, Al_2O_3, and Fe_2O_3, leading to C_2S and C_4AF formation rather than anhydrite. Along with the free CaO content, these compounds impart binding properties to the ash, as demonstrated in studies by Uibu et al. [13] and Arro et al. [24]. The portlandite ($Ca(OH)_2$) content is the highest in the ash fractions from the last collection points (collection points 8 and 9, Fig. 2), likely due to the lower temperatures and higher humidity in these sections.

Table 3. Mineralogical composition of the ashes from Auvere Power Plant, wt% [39]

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
Quartz SiO_2	3.6	14.3	12.5	12.7	10.8	10.6	6.6	5.3	3.1
Adularia $KAlSi_3O_8$	2.2	18.3	13.3	17.3	15.9	15.7	11.9	10.9	8.6
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	2.1	4.6	3.3	5.2	5.1	3.7	3.1	3.9	2.4
Calcite $CaCO_3$	35.0	15.4	12.5	10.0	10.8	17.7	18.1	9.5	9.6
Dolomite $CaMg(CO_3)_2$	5.1	n.d*	0.5	n.d	n.d	n.d	n.d	n.d	n.d
Lime CaO	18.4	16.0	19.2	19.4	20.3	9.8	10.1	9.1	<LOQ**
Portlandite $Ca(OH)_2$	2.0	0.9	1.3	1.0	1.0	4.8	6.3	17.8	14.6
Periclase MgO	7.0	5.3	6.8	5.6	5.4	5.3	5.3	4.9	7.7
Anhydrite $CaSO_4$	10.1	6.3	10.0	6.9	6.7	7.0	8.2	7.6	7.3
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	7.1	9.5	10.2	10.9	13.0	14.7	18.7	19.0	9.3
Merwinite $Ca_3Mg(SiO_4)_2$	3.1	5.3	5.2	5.9	6.4	6.6	7.8	8.0	5.3
Akermanite $Ca_2MgSi_2O_7$	3.6	2.3	3.9	3.2	3.1	2.1	2.2	2.1	8.8
Arcanite K_2SO_4	n.d	n.d	n.d	0.4	0.3	n.d	n.d	n.d	3.4
Sylvite KCl	0.3	n.d	n.d	n.d	0.3	0.3	0.4	0.9	0.6
Hematite Fe_2O_3	0.6	1.5	1.1	1.3	1.0	1.2	1.0	0.7	<LOQ

* n.d – not detected, ** LOQ – limit of quantification. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

The concentration of trace elements in the ash reflects their presence in the oil shale [21], which itself contains low levels of trace elements. As a result, trace element concentrations in the oil sale ash are also low, typically below 100 mg/kg, with some exceptions such as manganese (Mn), zinc (Zn), strontium (Sr), and titanium (Ti). As described by other authors [21, 40], trace element concentrations tend to be higher in finer ash fractions. However, some anomalies are observed – arsenic (As), Mn, and Zn have slightly higher concentrations in the bottom ash (Table 4). Lees et al. [41] conducted a similar analysis of trace element content across various oil shale ash fractions, including samples from Auvere PP, and obtained comparable results. Their findings confirmed that trace element concentrations remained low and did not exceed the regulatory limits set for soil [42].

Table 4. Content of trace elements in the ashes from Auvere Power Plant, mg/kg [39]

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
Li	6.6	23.4	18.3	26.2	24.5	25.4	19.7	16.8	11.2
Be	0.4	0.3	0.4	0.6	0.5	1.1	0.9	0.9	0.2
Ti	702	2843	2171	2947	2986	2959	2836	2692	2022
V	29.2	72.9	59.7	83.3	86.4	86.5	88.0	80.6	60.3
Cr	17.8	50.5	39.0	49.5	50.0	50.2	48.5	47.2	41.5
Mn	771	527	688	602	586	518	522	496	501
Co	4.0	6.8	5.8	7.1	6.9	7.5	7.1	6.6	5.7
Ni	18.9	32.0	27.5	33.4	32.0	35.6	32.5	30.5	27.1
Cu	3.9	9.2	7.6	9.9	9.7	10.1	9.7	9.1	10.1
Zn	235	151	171	173	145	158	126	117	116
As	53.4	22.2	39.9	27.5	28.2	31.2	37.0	35.8	43.8
Se	0.3	0.8	0.7	0.8	0.9	1.0	1.0	1.0	1.0
Sr	360	351	342	383	401	404	430	432	428
Mo	7.3	7.8	8.4	8.3	8.7	11.7	13.1	11.9	16.6
Cd	0.3	0.6	0.6	0.8	0.8	0.9	0.6	0.6	0.3
Sb	0.2	0.1	0.2	0.2	1.4	0.3	0.3	0.3	0.2
Tl	1.3	0.7	0.9	1.3	4.6	1.6	1.8	1.6	1.2
Pb	27.8	94.1	70.3	103	98.1	96.9	92.4	88.5	48.0

Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

As Auvere PP is the most recently built, its ash has received less attention than that of other power plants. However, Uibu et al. [13] conducted a study that contained a composition of oil shale ash from Auvere PP's ESP fields 1–5 and the overall ash from the main silo. Their findings indicate a higher calcite concentration in the total ash than in the ESP ash, supporting the hypothesis of a higher calcite concentration in the bottom ash. Furthermore, their report indicates an amorphous phase of 30% for Auvere PP's ESP ash and 12% for the total ash, rendering direct comparisons challenging. It also shows that the quality and characteristics of ashes are variable. However, some similarities and tendencies can be observed.

3.2. Eesti Power Plant CFBC unit

The 215 MW_{el} double-unit at Eesti PP was commissioned in 2004. The power unit was built at Eesti PP to replace a PC unit and consists of a predecessor modernised steam turbine and two circulating steam turbines with CFBC technology. The switch from PC to CFBC technology was primarily driven by environmental objectives, as CFBC technology achieves significantly better results in flue gas management, notably with substantially lower sulphur dioxide (SO_2) emissions. The characteristics and properties of Eesti PP CFBC unit are discussed extensively by Hotta et al. [43]. The primary fuel for the CFBC boiler is oil shale with a particle fraction of up to 20 mm. The average calorific value of the oil shale used is 8.4 MJ/kg. However, oil shale can be used in both forms: with lower calorific values, starting from 7 MJ/kg, and higher calorific values between 11.5–12 MJ/kg. It is also possible to co-combust retort gas from shale oil production. Figure 4 illustrate the layout of the plant and the primary locations where ash is collected. In case the unit operates at nominal load and uses 100% oil shale with a calorific value of 8.3 MJ/kg as fuel, the estimated ash flow is around 1 million tonnes per year.

The boiler's ash balance shows the distribution of combustion ash streams between all ash removal points and the stack (Fig. 5). The ash balance for Eesti PP CFBC unit has not been experimentally determined. However, since the boiler at Eesti PP CFBC unit is identical to that of Balti PP, for which an experimental ash balance has been established [36], the relative ash balance

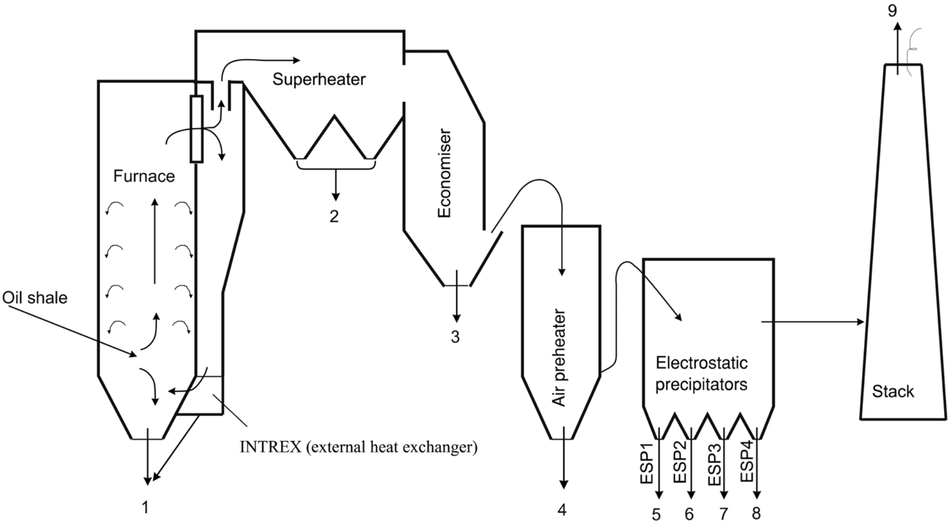

Fig. 4. Layout of Eesti Power Plant CFBC unit and ash collection points (adapted from [44]): bottom ash + INTREX (circulating ash) (1), superheater (2), economiser (3), air preheater (4), electrostatic precipitators – ESP1 (5), ESP2 (6), ESP3 (7), ESP4 (8), ash in flue gas (9).

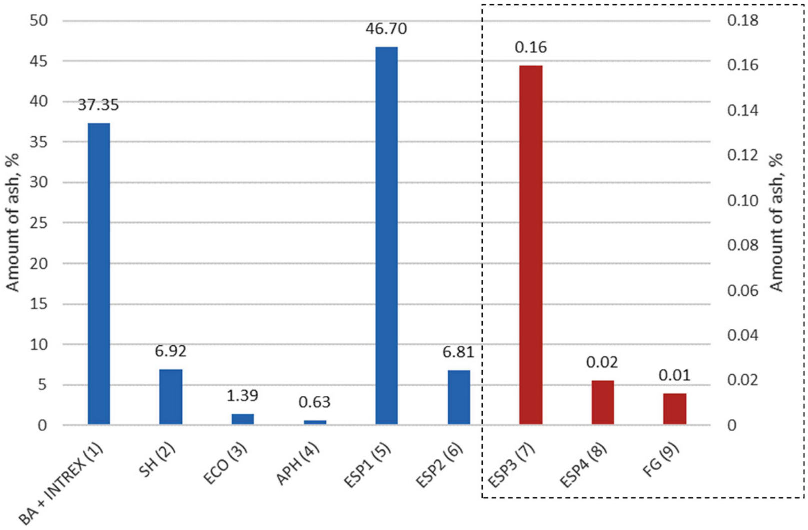

Fig. 5. Ash balance of Eesti Power Plant CFBC unit. Abbreviations: BA – bottom ash, INTREX – circulating ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

for Eesti PP CFBC unit is derived from Balti PP's data. The bottom ash from the boiler (which also contains circulating ash, the so-called INTREX ash) makes up about 37% of the total ash generated during combustion. Most of the fly ash is removed from the boiler by the ESP. The main part of the combustion ash is removed from the furnace. The share of the first field of the ESP in the ash fraction increases up to 49%. The amounts of fly ash leaving the stack are approximately 0.014% of the total combustion ash, which corresponds to a particle content in dry flue gases of about 20 mg/Nm^3 at 6% O_2.

The ash from Eesti PP CFBC unit has a chemical composition similar to that of Auvere PP's ash. Bottom ash contains the highest Ca concentration, exceeding 54%, while other fractions show Ca levels between 31% and 37% (Table 5). Similar to Auvere PP, Si concentration is lowest in the bottom ash. In contrast to Auvere PP, the free CaO content is generally lower, ranging between 14% to 19%, with the lowest levels found in the ash from the final stage of the flue gas cleaning system. This distribution aligns closely with the findings of Ots [21].

The mineral composition of the different fractions of Eesti PP CFBC ash also varies significantly (Table 6), with the most notable differences being the content of calcite, quartz (SiO_2), and adularia ($KAlSi_3O_8$). The bottom ash and ash in flue gas contain almost 40% of calcite, while it ranges between 10% and 17% in the other fractions. The bottom ash also contains modest amounts of quartz and adularia, whereas the other fractions exhibit significantly higher

Table 5. Chemical composition of the ashes from Eesti Power Plant CFBC unit, wt% [39]

	BA	SH	ECO	APH	ESP1	ESP2	ESP3	ESP4	FG
SiO_2	6.2	31.9	31.9	26.6	32.4	32.9	29.9	25.6	27.4
Fe_2O_3	2.7	4.1	4.1	3.8	4.3	4.3	4.6	4.6	4.7
Al_2O_3	2.1	9.6	9.9	8.3	10.3	10.6	10.3	9.4	9.1
CaO	54.5	31.5	32.3	37.3	32.5	32.0	32.7	34.4	34.2
MgO	4.4	5.7	6.0	7.1	5.6	5.8	6.4	6.7	7.1
Na_2O	0.03	0.1	0.1	0.1	0.2	0.2	0.1	0.7	0.1
K_2O	0.5	3.8	3.8	2.9	3.9	4.0	3.5	2.5	2.8
$SO_{3(total)}$	4.1	7.4	6.3	10.7	6.1	6.9	7.3	9.2	9.8
Cl	0.05	0.3	0.4	0.3	0.2	0.3	0.4	0.7	0.6
CaO_{free}	18.1	14.2	15.6	19.0	16.3	15.3	11.5	8.2	n.a*
CO_2	23.7	3.6	3.0	2.0	2.8	2.7	3.3	3.9	2.8
TIC	6.5	1.0	0.8	0.6	0.8	0.8	0.8	0.9	1.1

* n.a – not analysed. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

concentrations of these minerals. The content of C_2S/C_4AF is slightly lower than in Auvere ash but remains notable, particularly with higher concentrations observed in the ESP ash. Similar to Auvere PP's ash, anhydrite preferably forms in the bottom ash, while C_2S/C_4AF are more prevalent in the finer fractions. The content of dolomite ($CaMg(CO_3)_2$) and sylvite (KCl) is similar to that of Auvere PP's ash, while there are no traces of arcanite (K_2SO_4). Though in modest concentrations, hematite (Fe_2O_3), which is not found in Auvere ash, is present in almost all fractions.

Table 6. Mineralogical composition of the ashes from Eesti Power Plant CFBC unit, wt%

	BA	ECO	APH	ESP1	ESP2	ESP3	ESP4	FG
Quartz SiO_2	5.9	17.0	15.1	15.5	18.8	16.5	12.8	8.5
Adularia $KAlSi_3O_8$	4.3	17.1	11.8	15.1	16.6	16.9	15.4	6.4
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	<LOQ*	1.5	5.9	5.7	6.5	6.1	6.1	4.1
Calcite $CaCO_3$	35.9	11.7	10.3	12.7	12.4	11.7	11.5	38.8
Dolomite $CaMg(CO_3)_2$	3.1	n.d**	n.d	n.d	n.d	n.d	n.d	n.d
Lime CaO	8.2	5.8	10.5	11.6	6.2	4.0	1.9	5.0
Portlandite $Ca(OH)_2$	7.7	8.9	8.5	1.7	4.5	3.4	2.7	4.4
Periclase MgO	4.7	4.9	5.4	3.2	3.4	3.3	3.7	3.7
Anhydrite $CaSO_4$	15.7	11.6	14.0	11.2	9.7	10.9	13.3	9.9
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	6.5	8.9	8.6	13.8	9.3	12.1	15.8	5.8
Merwinite $Ca_3Mg(SiO_4)_2$	2.2	1.7	2.1	2.2	2.3	2.9	3.4	1.9
Akermanite $Ca_2MgSi_2O_7$	7.8	8.5	8.1	8.7	6.4	7.3	8.5	8.4
Sylvite KCl	<LOQ	0.5	0.6	n.d	n.d	n.d	n.d	n.d
Hematite Fe_2O_3	1.7	2.0	2.8	4.3	3.9	4.8	5.3	3.0

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

The trace element content is generally similar between the ashes from Auvere PP and Eesti PP CFBC unit, with the exception of As, lead (Pb), and Zn, which are significantly lower in the ash from Eesti PP (Table 7). At Auvere PP, the concentrations of As, Mn, and Zn are higher in the bottom ash, whereas in Eesti PP CFBC unit, only Mn shows an elevated concentration in the bottom ash. Reinik et al. [40] investigated trace elements in Balti PP CFBC ash, finding a trace element composition similar to that in the current study, with notably higher Mn concentrations in the bottom ash.

Bityukova et al. [23] examined the composition of various ash fractions from the CFBC units of Balti PP and Eesti PP, and their findings largely align with the results of the current study. Notably, while dolomite was not identified in the bottom ash from Eesti PP CFBC unit, it was detected in the bottom ash

Table 7. Trace elements content of the ashes from Eesti Power Plant CFBC unit, mg/kg [39]

	BA	ECO	APH	ESP1	ESP2	ESP3	ESP4
Li	1.8	40.3	30.2	38.8	29.7	37.7	29.4
Be	<LOQ*	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ti	885	4206	3190	4280	3167	3675	3237
V	17.0	72.7	56.2	75.1	72.0	80.2	76.3
Cr	16.7	70.4	55.1	73.9	66.0	74.4	73.9
Mn	821	757	797	590	492	479	447
Co	2.5	7.6	6.1	7.8	6.6	7.2	7.6
Ni	13.5	39.3	29.8	38.3	35.0	36.5	39.3
Cu	5.1	15.0	9.7	12.0	10.7	12.0	14.4
Zn	22.9	40.9	35.7	34.6	28.7	29.7	30.0
As	8.1	15.9	19.5	15.0	15.6	23.1	29.8
Se	n.d**	1.4	1.1	1.3	1.2	1.3	1.1
Sr	296	458	415	437	357	422	424
Mo	0.8	5.3	4.1	4.7	3.4	6.5	5.7
Cd	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sb	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	0.4	1.1	0.8	1.6	1.6	1.9	1.9
Pb	17.1	57.9	37.9	62.9	51.8	69.1	60.8

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash.

from Balti PP. Similarly, although wollastonite (CaO·SiO2) was absent in the ash fractions from Eesti PP, it was present in those from Balti PP. Since the CFBC technology is similar, and identical in both Balti PP and Eesti PP, these observations suggest that the differences in the mineralogical composition of the ashes are more significantly influenced by the quality and composition of the fuel used rather than by the combustion technology itself.

3.3. Eesti Power Plant PC unit with NID

Eesti PP's PC energy unit consists of a turbogenerator and two TP-101 type dust incinerators. The main steam parameters of boiler TP-101 are a steam production of 320 t/h, with main and intermediate superheated steam pressures downstream of the boiler at 13.2/2.2 MPa, and steam temperatures of 520/525 °C, respectively. The nominal gross power of the unit is 185 MW_{el}, and the unit efficiency is less than 30%. The boiler's efficiency at nominal capacity at steady state is between 86% and 88% [28]. The median particle size of the pulverised oil shale fed into the boiler through the burners is in the ranges from 45 to 55 μm, and the combustion of the fuel particles takes place at a boiler temperature of approximately 1400 °C. When operating at nominal load using 100% oil shale with a calorific value of 8.1 MJ/kg as fuel, the estimated annual ash production is approximately 0.9 million tonnes. However, the actual amount of ash generated can vary significantly depending on the unit's operating hours and the mix of fuels used. Notably, the unit can utilise shale oil retort gas for up to 80% of its heat input, which, combined with variations in plant availability, contributes to considerably lower ash outputs under different conditions.

Measurements of the ash balance carried out on this type of boiler [28] showed that the bottom ash represents approximately 42% of the total ash generated. The fly ash leaving the combustion chamber is divided between the other ash removal points as follows: 3.7% from the bottom of the superheater heating surfaces in the flue gas passage, 4.7% from the economiser (rising gas pass), 14.5% from the cyclone, 35% from the NID unit, and 0.02% from the stack.

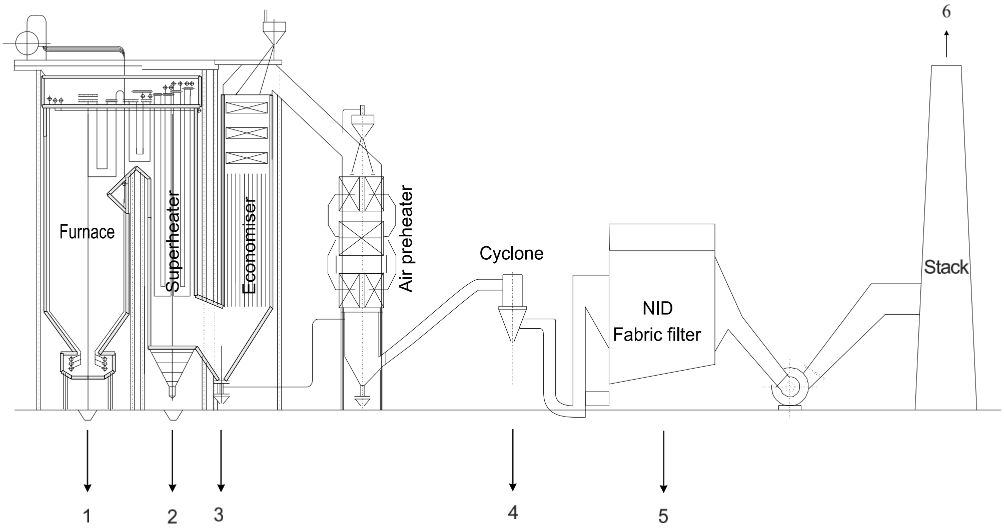

Fig. 6. Layout of Eesti Power Plant PC unit with novel integrated desulphurisation (NID) unit and ash collection points (adapted from [28]): bottom ash (1), superheater (2), economiser (3), cyclone (4), NID fabric filter (5) ash in flue gas (6).

The NID device incorporates a fabric filter for fly ash capture, which has a higher particle capture efficiency than an electrostatic precipitator. The measurement results show that fly ash in the flue gas leaving the stack from the NID unit is less than 20 mg/Nm^3, which allows for the calculation of the ash fraction coming from the NID unit.

The chemical composition of Eesti PP PC's ash (Table 8) differs from that of Auvere and Eesti PP CFBC ash. While Auvere PP's and Eesti PP CFBC's ash had lower Si content in the bottom ash, the PC ash had Si content rather unified ranging from 21% in the bottom ash to 26% in the fabric filter ash. Additionally, the free CaO content is the highest in the PC bottom ash, significantly exceeding the levels observed in CFBC ashes. A study by Konist et al. [28] reported a similar chemical composition for PC ash; however, this analysis was conducted prior to the installation of the NID device. The primary function of the NID is to reduce SO_2 levels in the flue gas. In the NID unit, free CaO binds with sulphur, which notably increases the sulphate content in the NID fabric filter ash.

The higher combustion temperature and finer particle size of oil shale in PC unit lead to an almost immediate decomposition of carbonates upon furnace entry. This rapid decomposition results in the formation of free CaO, which then reacts to form new minerals. [21] The mineralogical composition of ash fractions from Eesti PP PC is relatively unified, except quartz, anhydrite, and calcite in slightly higher concentrations in the NID fabric filter (Table 9). The mineralogical content of PC NID ash differs from CFBC ash mainly due to Ca containing minerals; the calcite content is significantly lower in PC NID ash while lime (CaO) and portlandite content are higher. In PC ash, the content of C_2S/C_4AF is significantly higher than in other ashes, which correlates with the findings of other authors [13, 24, 45] that PC ash has the best binding properties.

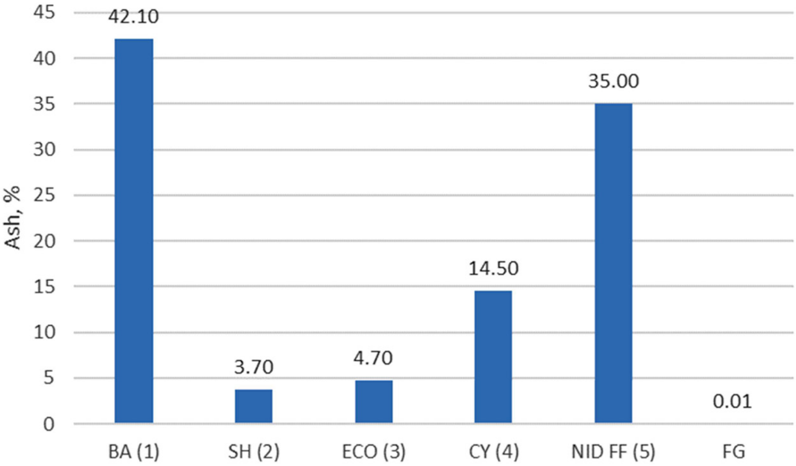

Fig. 7. Ash balance of Eesti Power Plant PC unit with NID. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash, FG – ash in flue gas.

Table 8. Chemical composition of the ashes from Eesti Power Plant PC unit with NID, wt%

	BA	SH	ECO	CY	NID FF
SiO_2	23.6	24.6	23.5	24.8	28.4
Fe_2O_3	3.7	3.8	3.7	3.8	3.1
Al_2O_3	5.3	6.4	6.2	6.7	7.4
CaO	52.1	45.1	45.8	48.8	33.7
MgO	7.6	7.2	5.8	6.1	38
Na_2O	0.2	0.06	0.08	0.08	0.2
K_2O	2.0	2.5	2.5	2.3	4.1
$SO_{3(total)}$	3.4	8.2	7.4	4.8	15.1
Cl	0.03	0.04	0.1	0.1	0.6
CaO_{free}	19.8	17.1	14.7	17.3	11.8
CO_2	1.86	0.84	3.87	1.40	4.12
TIC	0.51	0.23	1.06	0.38	1.12

* LOQ – limit of quantification. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

Table 9. Mineralogical composition of the ashes from Eesti Power Plant PC unit with NID, wt%

	BA	SH	ECO	CY	NID FF
Quartz SiO_2	3.5	6.7	6.9	6.8	10.5
Adularia $KAlSi_3O_8$	4.6	5.4	6.0	4.3	2.5
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	1.8	n.d*	n.d	n.d	1.2
Calcite $CaCO_3$	5.3	9.3	9.6	4.2	11.5
Dolomite $CaMg(CO_3)_2$	n.d	n.d	n.d	n.d	n.d
Lime CaO	24.6	19.8	21.1	24.6	8.8
Portlandite $Ca(OH)_2$	8.1	12.8	11.8	8.9	8.3
Periclase MgO	4.7	3.9	4.3	8.0	4.1
Anhydrite $CaSO_4$	3.8	8.0	6.2	9.5	11.8
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	20.9	14.4	15.6	16.5	18.8
Merwinite $Ca_3Mg(SiO_4)_2$	6.1	5.3	4.9	6.7	4.8
Akermanite $Ca_2MgSi_2O_7$	14.6	9.2	8.9	5.6	4.0
Sylvite KCl	n.d	n.d	n.d	n.d	1.2
Hematite Fe_2O_3	1.3	2.8	2.5	2.2	1.1

* n.d – not detected. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

The trace element content is relatively modest, with cadmium (Cd) and antimony (Sb) falling below the limit of quantification (Table 10). The concentrations of trace elements are fairly consistent across different fractions, resulting in somewhat higher concentrations along the gas passage. The levels of As and Pb in the samples were notably lower than those observed in the CFBC ashes discussed earlier. This difference can be attributed to the types of gas cleaning equipment used; CFBC plants utilised an ESP, while the current case employed a fabric filter. Previous research [21, 40] has also shown elevated concentrations of these elements in the ESP of PC power plants that lacked an NID system.

Table 10. Trace element content of the ashes from Eesti Power Plant PC unit with NID, mg/kg [39]

	BA	SH	ECO	CY	NID FF
Li	22.7	22.0	20.2	24.9	25.2
Be	1.1	<LOQ*	<LOQ	<LOQ	0.3
Ti	2306	2335	2406	2582	2848
V	42.5	46.2	48.1	51.7	55.4
Cr	36.5	39.4	41.5	46.2	57.4
Mn	744	667	706	783.2	454
Co	5.4	4.5	4.9	5.0	6.4
Ni	23.2	20.5	23.3	22.5	28.2
Cu	9.0	10.3	9.8	37.6	7.5
Zn	31.7	29.6	23.9	19.6	56.9
As	7.4	8.0	10.7	8.2	21.6
Se	0.7	0.9	1.0	1.0	1.0
Sr	397	352	387	418	297
Mo	1.3	n.d**	0.9	n.d	4.4
Cd	n.d	n.d	n.d	n.d	n.d
Sb	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	0.5	0.5	0.5	0.8	2.1
Pb	13.5	30.0	28.2	25.9	64.5

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

Bityukova et al. [23] analysed PC ashes from Balti PP and Eesti PP, which were not equipped with a NID system at the time of their study. They observed significant differences in the mineralogical composition of ashes from the two similar power plants, particularly in the composition of secondary calcium-bearing phases. The findings of the current study also indicate differences in the mineralogical composition of ash samples when compared to those reported by Bityukova et al.; specifically, the akermanite ($Ca_2MgSi_2O_7$) content was found to be notably higher, and melilite ($(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$) was not detected in the current samples.

3.4. Enefit280

Construction of a shale oil production plant based on Enefit280 technology started in 2012. Enefit280 is based on SHC technology, with a design capacity of 280 t/h for oil shale with a particle size of up to 6 mm. The main distinguishing feature of the Enefit280 technology, compared to other SHC-based technologies used in Estonia, is that the semi-coke produced during the pyrolysis process is combusted in an adiabatic CFB combustor [46]. When operating at nominal load, the estimated ash amount generated is 1.2 million tonnes per year. The layout of the plant and the primary locations where ash is collected are shown in Figure 8.

The combustion of the semi-coke in the combusting chamber takes place under adiabatic conditions in an oxidising atmosphere, the temperature in the furnace being kept below 800 °C with the basic objective of reducing the decomposition of carbonate minerals. The heat released from the semi-coke combustion in the boiler is primarily used to heat the retort solid material (solid heat carrier). Another part of the heat is used for drying the oil shale. The remaining heat, including the heat from cooling of the bottom ash and the gases leaving the furnace, is used to generate electricity through a steam cycle based on the Rankine cycle. However, the steam parameters are relatively modest compared to those used in the adjacent power plants. This results in the Enefit280 oil plant's relatively low electricity generation efficiency of around 26% [47].

The ash balance for Enefit280, presented in Figure 9, was indirectly obtained based on the technological parameters and the chemical analysis of ash gained at different points of the plant. At the same time, no direct measurement of ash discharge fluxes at different plant points has been carried out, and the actual ratios may slightly deviate from the presented values. The majority of the ash discharged from the boiler is bottom ash, comprising over 60% of the total ash produced. The next largest source of ash is collected from the utilisation boiler cyclone. The remaining ash is captured by the ESP, with only a very small fraction escaping as particulate matter in the flue gas.

The chemical composition of Enefit280 ash (Table 11) is similar to power plants' CFBC ashes, with a low Si content in the bottom ash and a significantly higher content in other fractions. However, unlike the ash from power

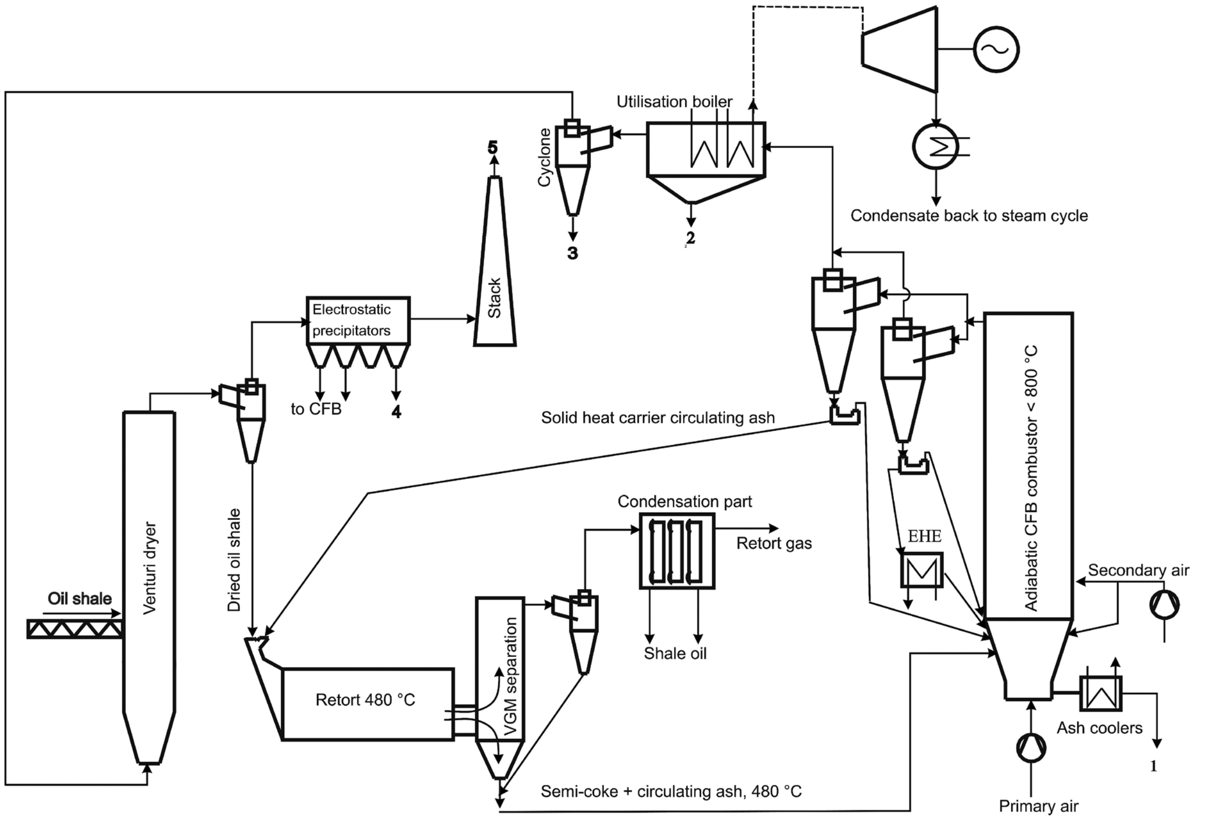

Fig. 8. Layout of Enefit280 technology and ash collecting points (adapted from [46]): bottom ash (1), utilisation boiler (2), cyclone (3), electrostatic precipitator (4), ash in the flue gas (5). Abbreviations: CFB – circulating fluidised bed, VGM – vapor-gas mixture, EHE – external heat exchanger.

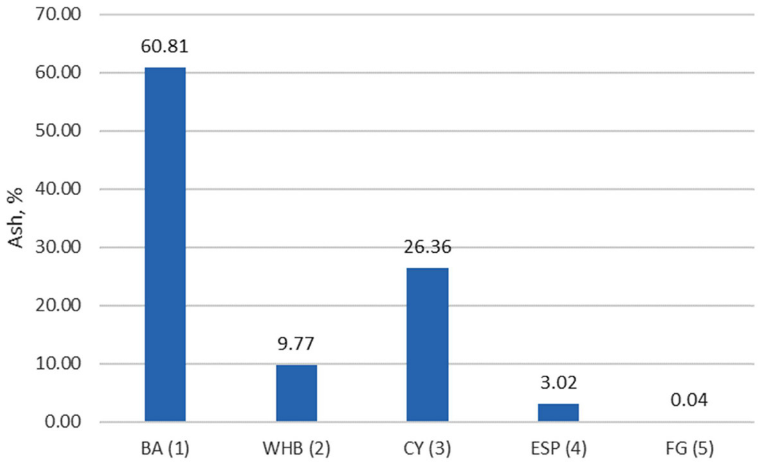

Fig. 9. The ash balance of Enefit280. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

plants, the free CaO content in Enefit280 ash is modest, around 1%. The limited amount of free CaO confirms that the low combustion temperature substantially reduces the decomposition of carbonate minerals. As a result, the mineralogical composition of Enefit280 ash is markedly different from that of power plant ashes. Specifically, Enefit280 ash contains higher concentrations of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), while exhibiting significantly lower ratios of C_2S/C_4AF ($Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$). Additionally, it contains almost no lime or portlandite, as shown in Table 12.

Table 11. Chemical composition of the ashes from Enefit280, wt%

	BA	WHB	CY	ESP
LOI	33.5	17.7	n.a	31.77
SiO_2	9.3	36.9	30.8	27.0
Fe_2O_3	1.6	4.5	3.3	2.8
Al_2O_3	1.3	11.1	6.7	7.5
CaO	45.6	23.0	29.5	22.2
MgO	3.2	2.5	3.2	1.7
Na_2O	0.04	0.2	0.2	0.1
K_2O	0.5	4.4	3.1	3.1
$SO_{3(total)}$	9.6	5.6	5.5	1.9
Cl	0.06	n.a*	0.08	n.a
CaO_{free}	1.1	n.a	1.8	1.04

* n.a – not analysed. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Table 12. Mineralogical composition of the ashes from Enefit280, wt% [39]

	BA	WHB	CY	ESP
Quartz SiO_2	3.4	16.8	16.0	14.9
Adularia $KAlSi_3O_8$	3.3	22.1	17.6	29.9
Muscovite $KAl2(AlSi_3O_{10})(F,OH)_2$	0.9	6.0	9.4	10.9
Calcite $CaCO_3$	57.6	29.3	32.4	20.4
Dolomite $CaMg(CO_3)_2$	14.6	6.6	3.4	5.0
Hematite Fe_2O_3	1.1	2.5	2.3	n.d*
Lime CaO	n.d	n.d	n.d	0.7
Portlandite $Ca(OH)_2$	0.5	n.d	n.d	0.6
Periclase MgO	3.1	2.8	2.1	1.0
Anhydrite $CaSO_4$	10.7	9.3	8.9	5.0
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	3.8	1.8	5.0	3.5
Merwinite $Ca_3Mg(SiO_4)_2$	1.3	0.8	1.4	0.6
Akermanite $Ca_2MgSi_2O_7$	0.7	1.9	1.3	2.2
Sylvite KCl	n.d	n.d	n.d	1.3
Chlorite	n.d	n.d	n.d	4.1

* n.d – not detected. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

The concentrations of trace elements in Enefit280 ash, as with ash from power plants, are relatively modest (Table 13). Consistent with CFBC ash patterns, trace element concentrations are generally lower in the bottom ash compared to other fractions, with the exceptions of Mn and Zn, which exhibit higher levels in the bottom ash.

Table 13. Trace elements content of the ashes from Enefit280, mg/kg [39]

	BA	WHB	CY	ESP
Li	6.2	19.1	21.8	22.3
Be	0.3	n.d*	0.7	n.d
Ti	572	2876	2817	3362
V	13.1	54.2	48.9	70.1
Cr	10.3	57.2	48.4	63.0
Mn	525	484	341	291
Co	2.8	5.9	6.8	8.3
Ni	11.9	25.1	33.5	30.1
Cu	3.0	8.3	8.0	9.7

Table 13. (continued)

	BA	WHB	CY	ESP
Zn	159	113	79.2	95.4
As	19.6	30.6	27.5	33.9
Se	0.6	0.9	0.3	0.9
Sr	352	346	332	215
Mo	4.2	15.5	12.5	22.5
Cd	0.3	1.2	n.d	1.4
Sb	n.d	n.d	n.d	n.d
Tl	0.8	1.6	n.d	9.6
Pb	18.5	121	52.5	102.2

* n.d – not detected. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Uibu et al. [13] analysed the chemical composition, mineralogical profile, and trace element content of bottom ash, cyclone ash, and total ash from Enefit280. Their findings are consistent with those of the present study, providing additional support and validation for its conclusions.

3.5. Petroter

The Petroter technology uses the SHC method to produce shale oil. Petroter has a capacity of 140 tonnes of crude oil shale (up to 25 mm) per hour (approx. 3000 t/day). The first Petroter unit was commissioned in 2009, followed by Petroter II in 2014 and Petroter III in 2015 [48]. The schematic diagram of the unit is shown in Figure 10.

Semi-coke combustion occurs in a reducing atmosphere (in the absence of oxygen) at a temperature of about 760–810 °C. The low combustion temperature, lack of oxygen, and relatively short residence time of the particles in the combustor determine the properties of the resulting ash. After combustion, the hot ash and gas mixture is split into two streams. One stream is directed to the heat transfer cyclones, where the ash is separated from the gas and retorted as a solid heat carrier. The second stream is directed to a three-stage ash cyclone, where ash separation takes place to clean the gas stream of solid material. A utilisation boiler is placed downstream of the ash cyclone (on the gas side), where the unburned organic components (H_2S, CO, VOCs, etc.) are combusted. The residual heat in the gas is utilised to dry the oil shale (Fig. 10) [47, 48].

The annual ash generated by the Petroter technology (all three units) ranges from 1.6 to 1.8 million tonnes [48]. The ash is removed from the process at two main separation points (Fig. 11): about 95% in the ash cyclones and about 5% in the ESP. A small fraction of the ash generated is emitted into the atmosphere.

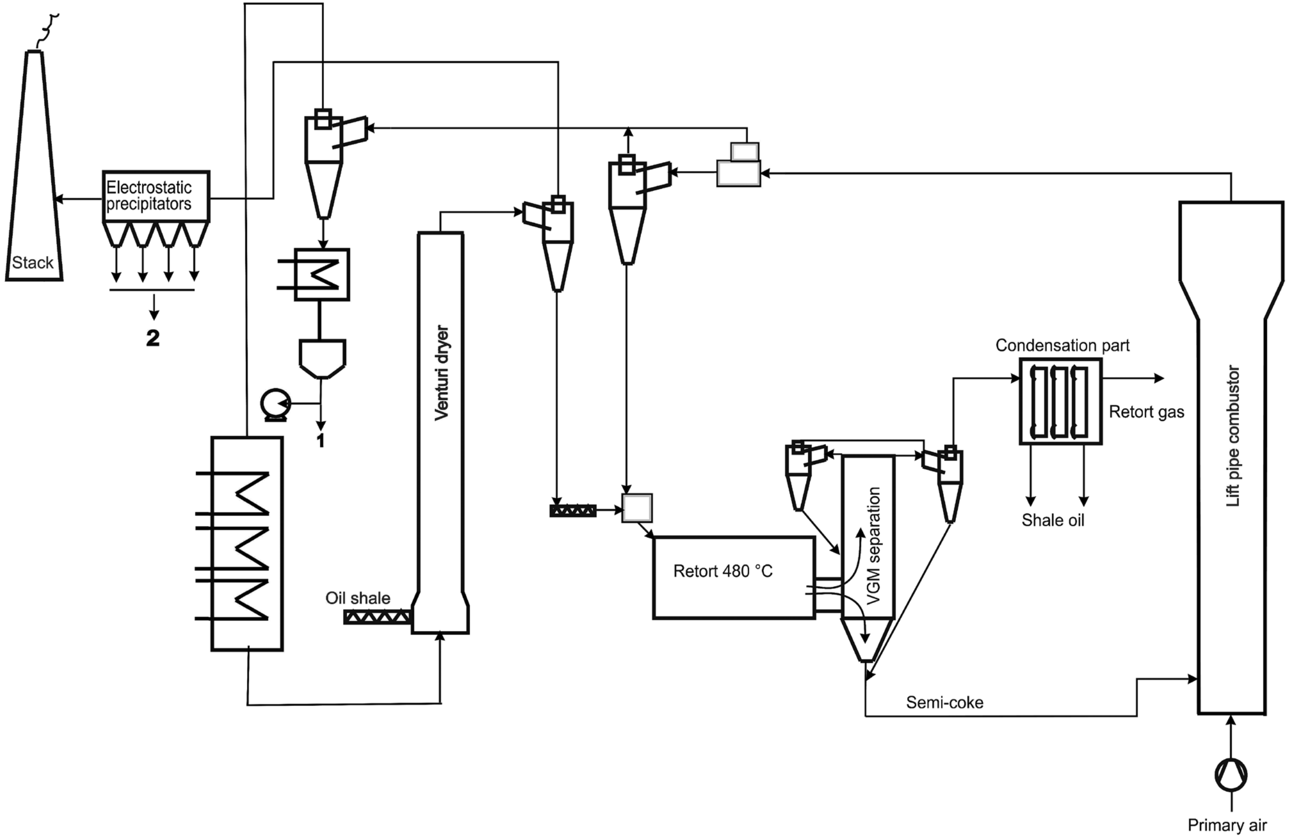

Fig. 10. Layout of the Petroter technology (adapted from [46]) and ash collecting points: cyclone (1), electrostatic precipitators (2), ash in the flue gas (3). Abbreviation: VGM – vapor-gas mixture.

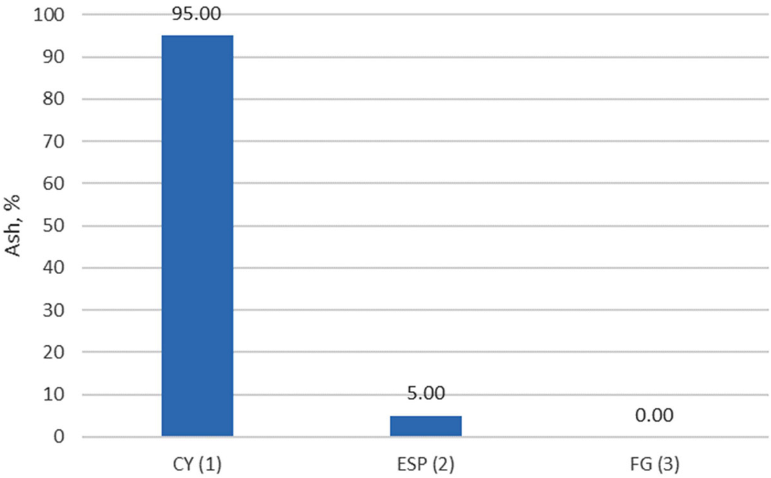

Fig. 11. Ash balance of Petroter ashes. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash, FG – ash in the flue gas.

The chemical composition of Petroter's ash varies significantly between the fractions from the cyclone and the ESP. Since the majority of ash is collected before reaching the ESP, the overall chemical composition of the total ash closely resembles that of the cyclone ash (Table 14). The low combustion temperature, lack of oxygen, and relatively short residence time of the particles in the combustor reduce the decomposition of carbonates, resulting in ash with minimal free CaO content. This limited free CaO content leads to a particularly distinctive mineralogical composition (Table 15). The concentration of dolomite ($CaMg(CO_3)_2$) is significantly higher than in any other ash fraction from other installations, while the content of muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$) is also notably high, especially in the finest fraction in the ESP (>38%).

Table 14. Chemical composition of Petroter ashes, wt%

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
LOI	26.7	16.6	23.5	24.4	24.5
SiO_2	19.1	40.3	21.8	20.3	26.0
Fe_2O_3	2.7	3.9	3.1	2.9	3.8
Al_2O_3	2.6	13.7	5.0	4.8	6.1
CaO	35.2	13.5	33.8	35.0	47.6
MgO	4.0	2.6	4.4	4.4	5.2
Na_2O	0.1	0.1	0.08	0.13	0.04
K_2O	1.4	5.2	1.8	1.7	2.4

Table 14. (continued)

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
$SO_{3(total)}$	5.2	4.2	4.3	4.0	4.2
Cl	0.1	0.02	n.a*	n.a	n.a
CaO_{free}	1.48	0.37	2.62	3.01	2.6

* n.a – not analysed. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

Table 15. Mineralogical composition of Petroter ashes, wt% [39]

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
Quartz SiO_2	10.5	11.3	14.1	9.9	11.6
Adularia $KAlSi_3O_8$	4.6	16.5	9.3	7.2	9.2
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	5.4	38.7	9.1	6.9	6.9
Calcite $CaCO_3$	50.2	20.0	43.0	44.7	48.4
Dolomite $CaMg(CO_3)_2$	14.3	1.0	10.8	19.7	10.3
Hematite Fe_2O_3	n.d*	0.5	n.d	n.d	n.d
Lime CaO	n.d	0.5	n.d	n.d	n.d
Portlandite $Ca(OH)_2$	0.6	0.8	n.d	n.d	n.d
Periclase MgO	1.7	<0.5	2.0	2.1	2.0
Anhydrite $CaSO_4$	2.9	1.2	2.3	1.4	2.5
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	3.7	0.5	0.7	0.9	0.8
Merwinite $Ca_3Mg(SiO_4)_2$	2.1	2.1	2.0	1.4	1.8
Akermanite $Ca_2MgSi_2O_7$	1.4	1.7	n.d	n.d	n.d
Oldhamite CaS	n.d	n.d	3.1	2.3	2.5
Magnetite Fe_3O_4	n.d	n.d	1.6	1.2	1.4
Apatite $Ca_5(PO_4)_3(F,OH,Cl)$	n.d	n.d	2.0	1.7	2.6

* n.d – not detected. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

The variation in the trace element content between the two ash fractions is considerable, with markedly higher concentrations observed in the ash from the ESP. As with the ashes from other installations described earlier, some discrepancies are evident; for instance, the concentrations of cuprum (Cu) and Mn are significantly higher in the ash from the cyclone.

Table 16. Trace elements content of Petroter ashes, mg/kg

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
Li	11.5	56.8	13.7	13.1	13.1
Be	0.4	2.4	0.9	0.8	0.8
Ti	1285	5640	n.a*	n.a	n.a
V	23.0	105.5	37.1	33.9	32.2
Cr	21.5	85.4	40.1	37.2	35.9
Mn	530	271	458	452	426
Co	4.0	11.9	4.5	4.3	4.1
Ni	15.3	41.4	20.4	19.0	18.6
Cu	78.7	9.0	9.7	7.1	6.2
Zn	37.3	35.2	47.2	35.4	36.4
As	6.4	8.7	8.7	7.8	7.2
Se	<0.2	0.5	1.2	1.1	1.2
Sr	264	245	256	245	259
Mo	1.4	3.0	n.a	n.a	n.a
Cd	n.d**	n.d	1.6	0.7	0.6
Sb	n.d	n.d	n.a	n.a	n.a
Tl	n.d	n.d	0.6	1.2	0.3
Pb	25.1	135	38.5	37.8	32.8

* n.a – not analysed, ** n.d – not detected. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

3.6. Leaching characteristics of ashes

The system pH of the ash eluates is significantly higher for ashes derived from power plants, with values around 13, compared to those from shale oil production facilities (Table 17). Notably, the eluate from the ash collected from the Petroter ESP exhibits the lowest system pH, measuring only 10.42. A clear correlation exists between the pH and conductivity, with higher conductivity observed in eluates with higher pH values. As CFBC ashes contain higher sulphur concentrations, sulphate (SO_4^{2-} ions) concentrations are highest in the eluates of CFBC ashes, as well as in those from the Enefit280 process, which also employs CFBC technology, and in the eluates of PC NID and fly ash. In contrast, leachates of ashes from PC furnaces and Petroter processes display significantly lower concentrations of SO_4^{2-} ions. Chloride concentrations (Cl^- ions) are lower in bottom ash eluates compared to finer fractions, with slightly higher levels in Enefit280 ashes and slightly lower levels in Petroter ashes.

The concentration of trace elements in oil shale ash from Estonian oil shale is relatively low, attributed to the depositional environment of kukersite oil shale, primarily composed of regular marine carbonate rocks rich in hydroxides and calcium. In this setting, trace elements did not accumulate significantly [49]. Therefore, the leaching of trace elements from the ash samples is minimal, with concentrations often falling below the limit of quantification. Even elements present in higher concentrations within the ash, such as Mn, Ti, and Zn, exhibit minimal leaching. While the majority of elements demonstrate leaching rates of less than 1 mg/kg, the mobility of Sr is notably higher, ranging from 8.94 to 57.24 mg/kg. It is particularly elevated in ash from power plants compared to that from shale oil production. Additionally, chromium (Cr) exhibits slightly increased mobility in Enefit280 ash and CFBC fly ash. Molybdenum (Mo) also shows marginally higher mobility in Enefit280 ash (Table 17). Similar findings regarding the mobility of Cr and Mo were also reported by Uibu et al. [13]

The mobility of trace elements in oil shale ash, when compared to the limit values set for waste acceptance at landfills in EU Commission Decision 2003/33 [50], demonstrates significantly lower levels than those established for inert waste, with the exception of Mo. Notably, while the chlorine ion content is lower in the eluates from bottom ash, the levels of chlorine ions in the eluates from fly ash, along with the sulphates found in all types of eluates, are below the thresholds for non-hazardous waste (Table 17).

Some trace elements, even at low levels, can pose significant risks to aquatic ecosystems. To protect the aquatic environment, the EU has established environmental quality standards (EQS) [51] for priority substances and certain other pollutants to protect water bodies. Among the trace elements analysed, Cd and Pb are classified as priority substances under current EU legislation, primarily due to their toxic effects on aquatic life, bioaccumulation potential, and persistence in the environment. Cd and Pb compounds are present in ash samples at marginal concentrations, with mobility less than 0.1 mg/kg for Pb and even lower for Cd. In contrast, Sr, Cr, and Mo, which exhibit higher mobility in ashes, are not currently listed as priority substances under EU legislation. The EU Commission has recently proposed a revision [52] to amend the list of priority substances, reflecting the evolving understanding of the environmental impacts of various chemicals. However, the revision does not include Sr, Cr, and Mo as priority substances.

Table 17. Release of components from ash samples at pH_{mat} (L/S = 10/1), mg/kg

	Auvere PP BA	Auvere PP ESP1	Auvere PP FA	Eesti PP CFBC	Eesti PP CFBC ESP1	Eesti PP CFBC FA	Eesti PP PC NID BA
Li	0.248	0.611	0.684	0.174	0.329	0.289	0.334
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ti	0.004	0.003	0.003	0.006	0.004	0.005	0.004
V	0.001	0.004	0.004	0.001	0.003	0.003	<LOQ
Cr	0.001	0.999	0.965	<LOQ	1.173	1.100	0.001
Mn	0.001	0.002	0.001	0.006	0.001	0.001	0.002
Co	0.003	0.002	0.002	0.002	0.003	0.003	0.002
Ni	0.010	0.007	0.006	0.008	0.008	0.008	0.006
Cu	0.003	0.006	0.015	0.003	0.010	0.005	0.011
Zn	0.060	0.026	0.023	0.009	0.015	0.013	0.016
As	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Se	0.004	0.034	0.036	0.009	0.034	0.032	0.002
Sr	39.08	54.38	57.24	26.50	35.08	38.22	51.81
Mo	**0.501**	**0.742**	**0.736**	**0.153**	**0.514**	**0.522**	0.143
Cd	0.002	0.003	0.003	0.002	0.002	0.002	0.001
Sb	0.002	0.001	0.001	0.001	0.001	0.001	0.001
Tl	<LOQ	0.048	0.046	<LOQ	0.037	0.030	<LOQ
Pb	0.000	0.110	0.103	<LOQ	0.041	0.053	0.003
Cl^-	420	**2550**	**2030**	330	**1980**	**2260**	210
SO_4^{2-}	**15406**	**8648**	**6651**	**14042**	**13770**	**14317**	**3622**
Conductivity, µS/cm	**10500**	**11840**	**10990**	**11200**	**9780**	**11000**	**9500**
pH	13.01	13.14	13.12	13.11	12.82	13.13	13.07

Table 17. (continued)

	Eesti PP PC NID FF	Eesti PP PC NID FA	Enefit 280 BA	Enefit 280 CY	Enefit 280 FA	Petroter CY	Petroter ESP	Limit value inert waste	Limit value non-hazardous waste
Li	0.279	0.247	0.103	0.117	0.113	0.189	0.122		
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ		
Ti	0.017	0.006	0.004	0.008	0.004	0.004	0.019		
V	0.004	0.002	0.102	0.161	0.171	0.024	0.460		
Cr	0.422	0.350	0.210	1.507	1.397	0.001	0.075	0.5	10
Mn	0.003	0.002	0.001	0.006	0.002	0.001	0.015		
Co	0.003	0.003	0.002	0.002	0.002	0.002	0.002		
Ni	0.009	0.008	0.004	0.006	0.004	0.004	0.005	0.4	10
Cu	0.013	0.004	0.003	0.016	0.005	0.020	0.018	2	50
Zn	0.012	0.010	0.002	0.018	0.006	0.024	0.036	4	50
As	0.003	0.002	0.010	0.008	0.012	0.005	0.024	0.5	2
Se	0.004	0.004	0.007	0.052	0.046	0.001	0.026	0.1	0.5
Sr	16.643	20.81	8.95	19.07	16.41	11.77	10.58		
Mo	0.460	0.376	**0.780**	**2.919**	**2.578**	0.407	**0.882**	0.5	10
Cd	0.002	0.002	0.006	0.008	0.007	0.002	0.003	0.04	1
Sb	0.001	0.004	0.005	0.001	0.001	0.002	0.007	0.06	0.7
Tl	0.047	0.041	0.000	0.004	0.007	<LOQ	0.077		
Pb	0.034	0.028	<LOQ	0.001	<LOQ	0.000	0.014	0.5	10
Cl^-	**2880**	**2640**	780	**1790**	**3700**	**930**	**900**	800	15000
SO_4^{2-}	**11730**	**13479**	**17708**	**11940**	**13975**	**5998**	**7230**	1000	20000
Conductivity, µS/cm	**11350**	**11650**	**3472**	**3240**	**3357**	**3321**	1980	2000*	30000*
pH	12.9	13.11	12.35	12.06	12.1	12.67	10.42		

* Conductivity is estimated as half of the total dissolved solids (TDS) value. Abbreviations: PP – power plant, BA – bottom ash, ESP – electrostatic precipitator ash, FA – fly ash, CFBC – circulating fluidised bed combustion, NID – novel integrated desulphurisation unit, FF – fabric filter ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Conclusions

The main aim of this study was to present detailed information about the different oil shale ash fractions generated in Estonia and to demonstrate significant variability in ash characteristics, depending on the technology and collection point in the process. Understanding these differences is essential for optimising the utilisation and valorisation of these ashes in various applications.

The distribution of ash fractions in circulating fluidised bed combustion (CFBC) power plants is notable, with approximately 30% consisting of bottom ash and 70% of fly ash. The first field of the electrostatic precipitator plays a pivotal role in this distribution, capturing about 50% of the total ash flow. In shale oil production, the distribution of ash fractions varies significantly between technologies. Enefit280 technology generates more than 60% bottom ash, leveraging its CFBC combustion process. In contrast, the Petroter technology produces exclusively fly ash, with most of it collected through cyclones.

Distinct differences between bottom ash and other fractions are observed, with notable variations in mineralogical composition and free CaO content. Pulverised combustion (PC) ashes exhibit a more uniform mineral composition across fractions, whereas CFBC ashes are more diverse in their chemical and mineralogical content. Differences in the mineralogical composition of ashes from similar technologies indicate that variations are influenced not only by the combustion technology used but also by the mineralogical content of the oil shale itself.

Ashes from power plants have a significantly higher free CaO content, reaching up to 31%, compared to ashes from shale oil production, which have a maximum of 3%. The presence of free CaO and compounds such as C_2S (Ca_2SiO_4) significantly enhances the binding properties of ashes from power plants. Free CaO, upon hydration, reacts with water to form $Ca(OH)_2$, which contributes to the pozzolanic and cementitious reactions by interacting with siliceous and aluminous components. Meanwhile, C_2S is a key hydraulic phase that undergoes slow hydration, forming calcium silicate hydrate (C-S-H) gel, which provides long-term strength development. These reactions are particularly pronounced in ashes from PC technology, where higher free CaO content leads to increased reactivity, as well as in finer fractions from CFBC plants. Consequently, these ashes hold potential for use in construction materials, such as binders or supplementary cementitious materials, thus improving their valorisation prospects.

Ashes from the shale oil industry have a fundamentally different mineral composition compared to combustion plant's ashes due to lower processing temperatures, which prevent the decomposition of carbonates. As a result, these ashes do not contain free CaO and lack significant binding properties. However, they remain a valuable resource for the extraction of calcium and other compounds, offering potential for various industrial applications.

The concentration of trace elements in oil shale ash mirrors their presence in the oil shale itself, which generally contains low levels of those elements. Consequently, trace element concentrations in the oil sale ash are also low, typically below 100 mg/kg. However, there are some exceptions, such as Mn, Zn, Sr, and Ti. As expected, trace element concentrations tend to be higher in the finer ash fractions.

The leachability test reveals that Cl^- ions leach significantly less from bottom ash compared to fly ash; however, this trend does not apply to SO_4^{2-} ions. For trace elements, the leachability is notable for certain elements such as Sr, Cr, and Mo. Despite their leaching potential, these elements are not classified as priority hazardous substances for the aquatic environment.

This variability in ash composition is influenced by factors such as fuel quality, combustion or processing technology, and the specific stage at which the ash is collected. These findings suggest that ash utilisation strategies could be tailored according to the specific properties of the ash fractions generated by each technology and process stage.

Data availability statement

Data are available on request from the authors.

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