

REVIEW

ABOUT THE MINERALOGICAL COMPOSITION OF ESTONIAN OIL SHALE ASH

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Results of previous research into the mineralogical composition of Estonian oil shale ash focused on using X-ray diffractometry, problems related to oil shale combustion, and utilization of oil shale ashes were analysed.

Introduction

The main mineral resource of Estonia – oil shale or kukersite – is used predominantly as a fuel in power plants. As Estonian oil shale (EOS) is rich in mineral matter, the amount of ash produced at its combustion is considerable. The substantial amount of ash and its particular physical-and-chemical characteristics cause numerous problems regarding power engineering, environmental protection and ash-applying industries. To solve the aforementioned problems, knowledge of the composition of EOS and its ashes is inevitable. While their composition by elements and oxides has been profoundly investigated, notably less research has been carried out regarding their composition in terms of chemical compounds or phase composition or mineralogical composition.

X-ray diffractometry (XRD) as a direct method to determine the mineralogical composition of ashes has been very rarely used. It was surprising to find in the beginning of this work how sparse the information on the analysis of ash composition was.

The aim of this paper is to provide a short overview about the results of investigations performed up to the current time with a special stress on XRD methods. Also problems concerning the application of fly ashes in energetics, environment protection, and the practical usage of ashes due to its mineralogical composition are discussed.

This overview is not a comprehensive one. It concentrates first on the results of preliminary investigations and thereafter on the specific applications.

Overview of Literature

In the middle of the 20th century, the use of Estonian oil shale increased sharply, resulting in intensified investigation on composition of oil shale and its ash. Chemical analysis (rational analysis), methods of petrography, XRD and thermal analysis, and technical analysis have been used [1, 2]. All these methods have deficiencies, and most of them are indirect. Only XRD allows a direct spectrum-based determination of the phase composition of the investigated material, using the respective databases. However, XRD leaves the so-called X-ray amorphous phase of ash outside the scope of the method.

The first investigators used rational analysis for determining the composition of EOS and its ash, using different solvents for treating oil shale [1, 3–7]. They presented chemical composition in percentages of oxide content, and on this basis the presumable mineralogical composition was calculated. The results were reported as chemical formulae but the actual minerals these refer to were not specified. Therefore these compositions can only provisionally be called mineralogical.

The main aim of the investigation was to find practical uses for the ashes. The binding properties of ash were of particular interest for producing building materials. The research in this area was conducted at Tallinn Polytechnical Institute (TPI, now Tallinn Technical University, TTU) (Kikas et al.) and at Building and Building Materials Research Institute of the Academy of Sciences of the Estonian S.S.R., BBMRI (Dilaktorski, Galibina et al.).

From the start, TPI’s main focus of investigation was the ash from pulverized EOS-fired boilers of the power plants (PPs). The ash was fractioned by specific gravity and particle size [8, 9]. The researchers of BBMRI studied the ashes formed at heating pulverized oil shale in a crucible at different temperatures and durations [10], as well as ashes from different boilers [7]. Great attention was paid to the determination of new formations resulting from combustion under different conditions [11].

Mets was the first to attempt direct determination of the phase composition of ashes by X-ray diffraction [12]. The minerals found by testing different

fractions of cyclone ash are shown in Table 1 (the notation used by the authors). In subsequent studies rational analysis was used. The phase composition of cyclone ash from Kohtla-Järve PP calculated by Piksarv [1] is presented in column 2 of Table 1.

In his research [13], Dilaktorski summarised conclusions of earlier petro-

Table 1. The Minerals Found in EOS

Mets, Kikas [14]	Piksarv [6]	Dilaktorski [15]
α -2CaO · SiO ₂	β -2CaO · SiO ₂	2CaO · SiO ₂
CaO · Al ₂ O ₃	CaO · Al ₂ O ₃	CaO · Al ₂ O ₃
CaO	CaCO ₃	2CaO · Fe ₂ O ₃
MgO	CaSO ₄	CaO
Quartz SiO ₂	CaO	MgO
FeO	MgO	CaSO ₄
	CaS	CaS
	FeS ₂	CaCO ₃
	CaCl ₂	

graphical studies [10, 7] on EOS and the minerals found in its ash. The mineral part of EOS can be divided into two: carbonate and aleurite/clay. The latter may, in turn, be divided into terrigenous and authigenic parts. Dilaktorski identified more than 20 minerals by microscope, many of which appearing only as single crystallites.

During the combustion in furnaces and thermal processing of oil shale, sophisticated chemical and physical processes take place, which result in radical difference in the composition of the formed ashes from that of oil shale. High temperature causes compounds to decompose; the resulting components may react and give new compounds, or remain inert. Some particles of the initial compounds may not decompose.

Different processing methods give ashes of different composition. At pulverized combustion it is important to take into account temperatures as well as duration of keeping the particles in the heat zone. Particle flow by flue gases and separation in cyclones and electrostatic precipitators should also be considered, as ashes collected from different nodes have different composition. Dilaktorski detected more than 30 compounds in different types of ash, with some new formation crystallites unidentifiable in microscope due to their small size. The results of pulverized EOS combustion can be summarized as follows [13]:

The larger particles (over 40–50 μm) contain pieces of lime as well as a mixture of calcium and magnesium oxide. In time, the lime partly hydrates to portlandite and partly carbonizes to calcite.

The mineralogical composition of the finer particles varies considerably:

- Compounds resulting from complete fusion of clay and clay-lime minerals and from decomposing, fusing and oxidation of marcasite.
- Particles of non-fused quartz, orthoclase, plagioclase, mica, as well as some lime and portlandite.
- Partially fused particles of glass and crystalline phase.

Glass-phase particles are of different composition, some of them containing the residue from undissolved minerals (quartz, orthoclase, lime). The insoluble residue contains crystals of rutile, leicoxene and zircon.

The following new formations were found: dicalcium silicate $\beta\text{-Ca}_2\text{SiO}_4$, calcium silicate $\alpha\text{-CaSiO}_3$, a mineral of melilite group, pyrrhotite Fe_{1-x}S , hematite, magnetite, calcium ferrites, the mixed sulfates from calcium and potassium, and calcium aluminate $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The same Table also contains mineralogical composition calculated using the rational analytical method (column 3). Compared to the research of Piksarv [1], $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ is added, CaCl_2 is absent, and FeS_2 is replaced by Fe_{1-x}S .

With the development of power plants, the focus of research has shifted. The first studies dealt with the ashes from the cyclone of Kohtla-Järve Combined Power Plant, CPP (to a lesser extent also the furnace bottom ashes) [1, 8, 9] and the ash of Ahtme CPP. Since the beginning of 1959 attention was

focused on the ashes from Baltic PP [14–21]. As different blocks of Baltic PP have different boiler and ash-handling systems, it was essential to enable fast determination of the composition of ashes. This was done in the studies mentioned above, concentrating on cyclone ash in the earlier studies and electric precipitator ash in the later ones. The workgroup of Kikas continued fractioning fly ash by specific gravity and by particle size. Fly ash was divided into three fractions according to the particle size: coarse – mainly 30–150 μm , fine – 10–30 μm and the finest one – smaller than 15 μm (mainly smaller than 10 μm). The composition of each fraction was determined in oxide percentages, and the content of main minerals was calculated. The glass phase [22] and the insoluble component [20] were studied separately.

Galibina analysed the ash collected from various nodes of the ash-handling system [14]. A separate study of cyclone and electrostatic precipitator ashes of the boilers TP-67 of block No. 4 was carried out [21]. According to the particle size, the ashes were classified as follows: less than 50 μm , 50–100 μm and above 100 μm . Due to the absence of Sobolev cameras in these boilers, the flow of coarse particles into electrostatic precipitators was observed, especially into the first field of the precipitator. In the following precipitator fields the share of the fine fraction increased continuously. For some oxides, the possible range of content was determined.

Compared to the cyclone, CaO and free CaO content in the first field of the electrostatic precipitator was higher, decreasing continuously throughout the following fields. The figures regarding silicon oxide showed a converse tendency – the first field of the electrostatic precipitator contained less silicon oxide than the cyclone, with its content increasing along the precipitator. The content of SO_3 increased along the ash duct. To compare, it can be added that based on the studies of Kikas et al., the finer the particles the lower their lime content, but the higher their anhydrite and potassium dioxide content [19].

As to the research of the ashes of Estonian PP, the situation is different. The boilers installed at Estonian PP are, in principle, of the same type as those in the block No. 4 of Baltic PP, except for being twin boilers TP-101. No research results on Estonian PP ash, comparable with the aforementioned investigations on the ash of Baltic PP, have been published. The reports on research activities of the Building Materials Research Laboratory of TPI [23] presented only technical parameters of the ash fractions for determining their binder properties. They show that the parameters of ashes from boilers 1–4 and 5–8 differed considerably. It was concluded that the electrostatic precipitator ash of Estonian PP is not fit for manufacturing Portland cement. Thus the building material developers and other utilizers of oil shale ash retained their interest only in the ash of Baltic PP. Consequently, the later utilization of ash in Estonian industries as well as in agriculture was mainly based on the ash from Baltic PP [24].

Apart from the ash of Baltic PP, chemists and power engineers still continued studying the ash of Estonian PP. The studies at the Department of

Thermal Engineering of TTU presented ash balances for both PPs, also the content and amounts of the 11 “macrocomponents” (oxides) and 45 microelements in their ash in the period of 1981–1992. The analyses were outsourced from several institutions using chemical analysis, different methods of spectrum analysis and analysis by neutron activation.

None of the published researches contained data about the phase composition of fly ash permeating the atmosphere.

The methods of XRD have been surprisingly underexploited in the studies of the mineral compositions of kukersite and its ashes. As mentioned before, the first to use roentgenography in the study of ashes was Mets in the beginning of the 50s [12]. The Debye-Scherrer registration method was used in the research and the roentgenogram was recorded on the photo film. The aim of the study was developing a method but, unfortunately, the research did not continue. However, XRD was used within the following decades for detecting the cement minerals formed in the course of ash processing (see [11, 25]).

Beginning from 1977, Utsal applied the XRD method for studying EOS [26, 27] using X-ray diffractometer DRON-0.5 (interval $1\text{--}45^\circ$ of angle Θ) connected to a PC. The authors of [27] present the distribution of the main components of kukersite – organic matter, carbonaceous and terrigenous minerals – in the profiles of the Baltic deposit. Carbonaceous minerals are represented by calcite and, in smaller quantities, also dolomite; terrigenous minerals by quartz, feldspar, hydromica (illite?) and chlorite, and authigenic minerals by pyrite. It should be noted that in the modern database of chemical compounds the names of minerals used – feldspar, hydromica, chlorite – each denotes a group of minerals.

Utsal also used the XRD method to study ash, but the ash produced from kerogen concentrate heated at the temperature 500°C [26].

Pets has also conducted XRD research on EOS and its ash [28, 29]. Measurements were made in the University of St Petersburg by X-ray diffractometer DRON-2.0 with the interval $15\text{--}60^\circ$ of angle 2Θ , in the working condition: voltage 35 kV, anode current 10 mA, detector's velocity $2^\circ/\text{min}$, range of sensitivity 100 imp/s, time constant 5 s. The range of minerals detected in kukersite by XRD could not be enlarged. The samples of furnace bottom ash and fly ash, collected from all nodes of the ash-handling system, including chimney were studied (the calculated content of seven main elements in nature and a secondary-rate element Ti are given only for the furnace, steam superheater, cyclone and the 1st and 4th fields of electrostatic precipitator). Unfortunately, the data about minerals and their behaviour in the ash-handling system are rather limited. It is claimed that:

- All samples show calcite and dolomite, the content of both decreasing along the duct. In the furnace they partially decompose, forming oxides of micro- and macroelements.
- Calcium oxide sulfatizes into gypsum. The furnace bottom ash does not contain much gypsum, but its content increases in fly ash.

- Magnesium oxide carbonizes into magnesite. Its content increases continuously along the duct.

Residues formed at the combustion of oil shale include: ash to ash fields and to consumers, and emissions from the chimney in the form of fly ash, aerosol particles and vapour/gas. The amount of ash formed at the combustion of oil shale in Estonian power plants is enormous. The results of the Department of Thermal Engineering of TTU [24, 30] show that in the first half of the 1980s the four oil-shale-fired PPs of Estonia (Estonian, Baltic, Kohtla-Järve and Ahtme) utilized ca 25 Mt of oil shale per annum producing 11 Mt of ash. In the 1990s the amount of oil shale burnt and, consequently, the amount of ash produced was constantly decreasing. In 1992 17.6 Mt of oil shale was burnt producing 8.0 Mt of ash. In 1995 the amounts were 12.2 Mt and 5.5 MT, respectively.

The atmospheric emissions of EOS-fired power plants in North-East Estonia have caused concern in Estonia as well as in Finland. The main reason for that is an extremely high air pollution by fly ash and acidic components of flue gases, especially sulfur oxides, spreading often over the territories of neighbouring countries – Russia and Finland. Appearance, spreading and effects of the pollution have been investigated in several researches.

EOS contains a considerable amount of microelements, several of them harmful. The microelement content of EOS and its ash, and their distribution in the environment have been thoroughly investigated by Pets and her colleagues (see references in [28, 29]). It should be taken into account that along its path through the ash-handling system ash is enriched with harmful microelements, and the emissions from the chimney contain a considerable amount of these. Generally, the content of microelements in fly ash emissions ranges from a couple to dozens of grams per ton [31].

Quantitative estimation of the distribution and precipitation of contaminants has been given using the method of mathematical modelling. In [32], individual elements of pollution, deposited into Estonian water basins and on dry land, are calculated. The average calcium load was taken as the basis to calculate loads for 55 elements present in fly ash. Contamination with harmful microelements on dry land can amount to 100 mg/m² per day.

Concerning several other contaminants, the situation is much more complicated. During the Soviet era, nature protection was split between different governmental agencies, and much of the data was kept secret. The available data are often incomplete and contradictory. The comparison of data is hindered by the fact that many of the publications do not mention the method used for obtaining the data or give no reference to the source. Inconsistencies in data continue into the publications of the 90s, especially regarding atmospheric emissions of fly ash and gaseous residues from oil shale combustion. TTU thermal power engineers and the researchers of Institute of Chemistry of the Estonian Academy of Sciences have published the data on the content of harmful gases (CO₂, SO_x, NO_x, HCl) in the residuals, ash in the flue gas emissions and carcinogenic polycyclic aromatic hydrocarbons.

Using the results of laboratory experiments, manual measurements at PPs and data from technical analysis, the concentrations of these substances in flue gases and amounts in emissions have been determined [33–35]. Data on pollution by PPs have also been published by environmental scientists [36–38]. The aforementioned sources, annual reports from the proprietors of the pollution sources and the results of air analyses have been used.

To gain a comprehensive overview of PPs emissions, Finnish researchers carried out extended measurements in Estonian PP in Sept. 1992, and in Baltic PP in May 1993 [39], using methods based on the measurement technology used in Finland. Both continuously operating instruments as well as manual measurements were used. The concentrations of NO_x , CO, C_xH_y , HCl, HF and polycyclic aromatic hydrocarbons in flue gas were found to be relatively low and acceptable according to German emission limits [40]. In spite of significant sulfur capture (average values for different boilers ranging between 68 and 77 % of the initial sulfur content of the fuel), SO_2 concentration in flue gases still remained very high (average 1500–2600 mg/m^3 , 10 % O_2 ; the limit of the German emission standard being 300 mg/m^3).

Particle emission of the Estonian PP estimated by VTT Chemical Technology was two and a half times higher than the corresponding value declared by *Eesti Energia* (Estonian Energy) in 1992, estimates converged better for Baltic PP. All the particle concentrations measured at both power plants (1440–6250 mg/m^3 , 10 % O_2) were remarkably higher than the German emission standard (40 mg/m^3 , 10 % O_2) permits. The particle size distribution, measured together with the total dust emission, demonstrated that even large particles penetrate the electrostatic precipitators in large numbers. Low efficiency of particle control devices leads to remarkably high emissions of heavy metals. The average particulate heavy metal concentration in the flue gases of the Baltic PP exceeded the German emission standard moderately, but in the case of the Estonian PP – three times.

Emissions of particles by Estonian power plants in 1992 are presented in Table 2.

Table 2. Yearly Emissions of Particles from Estonian Power Plants (tonnes per year) in 1992

Determined by	Estonian PP	Baltic PP
VTT Chemical Technology [39]	112,300	74,000
Department of Thermal Engineering of TTU [24, 31]	105,000	89,000
Environmental scientists [37, 38]	43,773	85,985

Analogously to the concentration of pollutants in flue gases, the amounts of pollutants calculated in [39] also differ from the previous results. In 1992, the annual emission of SO_2 was 138,000 t, which is bigger than the 129,000 t suggested by *Eesti Energia*, but considerably less than the usual Finnish estimation (250,000 t).

The researchers of the Department of Thermal Engineering of TTU explain [24, 31] the differences in the analyses of particle emissions made in Finland from those made earlier in Estonia as follows: in PPs particle emissions were analysed using the filter method, in that case the dimensions of the particles caught by the filter exceed 5–10 μm , while particles of smaller dimensions pass the filter. All researches on ash fractions have established that fly ash going to the chimney contains a considerable amount of particles under 5–10 μm .

According to [24, 31], chimneys emit “fly ash” and “aerosol particles”. The former constitutes 1.5 % of all ashes produced by the boiler; the latter is estimated to amount to about 1 %. The estimations about both PPs (see Table 2) differ from the results given in [39] but the differences are not significant. In clarification, “aerosol particles” here denote solid particles. To compare, the Table also presents the data of the environmental scientist [37, 38] regarding “solid anorganic pollution (fly ash of oil shale)”, which considerably differs from the aforementioned data about Estonian PP. The latter data have allegedly been used in estimating the spread of air pollution and pollution load in North-East Estonia [38]. Hence the question: how veracious are the data?

As mentioned above, in the 90s the burning of oil shale decreased. Consequently, the amount of pollutants in the air also decreased. According to the data presented in [38], the rapid fall continued until 1995, since then no significant decrease in the pollution level has been noted.

In connection with pollution problems it should be reminded that burning oil shale releases enormous amounts of carbon dioxide (CO_2). Burning 1 kg of EOS releases ca 0.99 kg of CO_2 [34]. Thus, in 1992, the Estonian PPs “produced” ca 17.6 Mt CO_2 . (1992 has been chosen for presenting numerical data as this is a year we have data about to compare).

A special edition of *OIL SHALE* [41] is dedicated to research into oil shale mining and the impact of its combustion residues on the environment. Detailed studies of the landscapes in North-East Estonia demonstrate vividly the result of human consumption: the increase in the content of some heavy metals in the upper part of peat layers is as much as 20 times higher than their background values, and the lacustrine sediments formed during the last 50 years contain much higher concentrations of almost all chemical elements. Disturbances in the ecosystems can be traced to the sharply increased atmospheric fluxes – alkanization, disturbances of the plant cover on the peatbogs, essential changes in the fauna in the lakes, and degradation of the forest.

Oil shale combustion involves complex technical problems, which arise from the special characteristics of oil shale [42–45]. EOS is a solid fuel with high content of mineral matter (60–75 %), moderate moisture content (11–13 %), and low heating value (net heating value of moist fuel 8.5–9 MJ/kg). Chlorine combined with the organic and mineral matter of shale is also one of the specific features of EOS. The major problem in the operation of steam

boilers fired with pulverized oil shale is the intensive fouling of the furnace wall tubes and convective heating surfaces with bounded ash deposits, as well as their high-temperature corrosion and wear.

The fouling intensity of the boiler heating surfaces, while burning oil shale, is associated not only with high content of mineral matter of the fuel, but mostly with the complicated composition of ash formed in the course of the burning process. Oil shale ash also possesses a very high corrosion activity. The main reason of that lies in the presence of potassium chloride [46–48], synthesized in the course of combustion by the chlorine of shale kerosene and by potassium volatilized from the alkali-bearing ash constituents. The wear of high-temperature heating surfaces is also associated with high-temperature corrosion.

Part of oil shale ash is utilized in building materials industry, agriculture, road building and chemical industry. Kikas and Öpik have dealt with the questions of rational use of the ashes [49–51].

Due to its binding properties the ash is utilized in building material industry in producing high-quality and special Portland cement, medium-quality cement, autoclaved concrete and heat-insulating material. Portland oil-shale cement is of utmost importance, as on the basis of this several regular as well as pretensioned concrete products and constructions have been built and buildings erected. Due to its binding properties ash is also applicable in road engineering.

The lime-rich EOS ashes are used as lime fertilizers and neutralizers in agriculture [52]. Pulverized ash is easily obtained from thermal power plants being a residue of the production. Dry, ideally fine for using as a lime fertilizer, with great neutralizing capacity, it contains in addition to Ca considerable amounts of K, Mg and S as well as small quantities of microelements (Cu, B, Mn, Co, Zn) needed for plant nutrition.

In the 90s, the delivery of Estonian PP ashes to consumers unfortunately decreased [24].

Sulfur oxide is still a significant air pollutant from PPs, although much of it is bound in the ash-handling system. Solid wastes formed at the EOS-fired power plants have a considerably high reactivity towards SO_2 , therefore they could be applied as potential sorbents for further desulfurization of flue gases [53, 54]. The results of the industrial-scale experiments at the Baltic PP confirmed the efficiency of using cyclone ash and mud in recycling the CO_2 emission by combustion of powdered EOS.

Conclusions

Little research has been performed on the mineralogical composition of Estonian kukersite ash, and even less data is available about the ash of Estonian Power Plant.

The existing data are scattered in literature.

The published data on pollutants resulting from oil shale combustion are controversial.

It is essential to investigate the mineralogical composition of Estonian oil shale ash systematically by X-ray diffractometry method.

REFERENCES

1. *Piksarv E.* On the mineralogical composition of cyclone ash obtained at combustion of pulverized kukersite oil shale, and of ash fractions // *Transact. Tallinn Techn. Univ.* 1959. No. 166. P. 129–149 [in Russian].
2. *Kattai V.* Elemental composition of oil shales from the major deposits of the European part of the USSR // *Oil Shale.* 1989. Vol. 6, No. 2. P. 117–132 [in Russian, Summary in English].
3. *Torpan B.* On the chemical and mineralogical composition of kukersite // *Transact. Tallinn Techn. Univ.* 1954. No. 57. P. 22–31 [in Russian].
4. *Galibina E.* Процессы минералообразования, происходящие при нагревании неорганической части кукурсита и твердении сланцевых смол (Processes of mineral formation occurring at heating kukersite inorganic part and hardening of oil-shale ashes) : Thesis of Ph.D. dissertation. 1956 [in Russian].
5. *Piksarv E.* On the alkaline compounds in the cyclone ash // *Transact. Tallinn Techn. Univ.* 1959. No. 166. P. 150–162 [in Russian].
6. *Mändmets H.* Analysis of mineralogical components of kukersite oil shale ash // *Studies on Building.* Tallinn, 1961. P. 129–142 [in Russian, Summary in English].
7. *Dilaktorski N., Galibina E., Kiiler M.* On the composition of ash obtained at combustion of kukersite dust and the binding properties oil shale ash glas // *Studies on Building.* 1961. P. 113–128 [in Russian, Summary in English].
8. *Kikas V.* Fractional composition of cyclone ash of pulverized oil shale boiler // *Oil Shale Ash in Building.* Tallinn, 1955. P. 58–66 [in Russian].
9. *Kikas V.* Binders from kukersite oil shale ash // *Transact. Tallinn Techn. Univ.* 1959. No. 166. P. 5–28 [in Russian].
10. *Dilaktorski N., Galibina E.* About the processes of mineral forming by heating of oil shale ash and hardening of hydrated products of combustion // *Oil Shale Ash in Building.* 1955. P. 31–46 [in Russian].
11. *Galibina E., Dilaktorski N.* The mineralogical composition of oil-shale ashes hardening at normal and heightened temperatures and pressures // *Studies on Building.* 3. Tallinn, 1962. P. 46–59 [in Russian, Summary in English].
12. *Mets G., Kikas V.* The use of the methods of X-radiation for the study of the mineralogical composition of oil shale ash // *Oil Shale Ash in Building.* 1955. P. 89–94 [in Russian].
13. *Dilaktorski N.* Theoretical basis for the utilization of the mineral compound of oil-shale in building materials industry // *Studies on Building.* 3. 1962. P. 5–45 [in Russian, Summary in English].
14. *Galibina E.* Composition and properties of oil shale ash from Baltic TPP // *Studies on Building.* 4. Tallinn, 1967. P. 3–13 [in Russian].

15. *Galibina E., Veretevskaja I.* The changes in the composition and properties of oil shale ash from Baltic TPP // *Studies on Building*. 7. Tallinn, 1967. P. 39–44 [in Russian].
16. *Kikas V., Kogermann E.* The ash precipitators at the Baltic Power Plant and the kinds of the fly ash, being caught in it // *Transact. Tallinn Techn. Univ.* 1968. No. 272. P. 3–13 [in Russian, Summary in English].
17. *Kikas V., Hain A., Reispere H.* The physical-and-chemical and binding properties of kukersite oil shale fly ash fractions // *Transact. Tallinn Techn. Univ.* 1968. No. 272. P. 29–47 [in Russian, Summary in English].
18. *Hain A., Kikas V.* The physical and binding properties of the finest fraction of kukersite oil shale fly ash // *Transact. Tallinn Techn. Univ.* 1968. No. 272. P. 89–101 [in Russian, Summary in English].
19. *Kikas V., Otsman R.* The use of kukersite oil shale ash fractions in building material industry // *Transact. Tallinn Techn. Univ.* 1970. No. 296. P. 35–45 [in Russian, Summary in English].
20. *Nurm V., Kikas V.* About the properties of insoluble residue of oil shale ash // *Transact. Tallinn Techn. Univ.* 1971. No. 308. P. 3–13 [in Russian, Summary in English].
21. *Veretevskaja I., Galibina E.* The composition and properties of oil shale ash from boilers of 4th block of Baltic TPP // *Studies on Building*. 9. Tallinn, 1968. P. 106–113 [in Russian].
22. *Nurm V., Piksarv E., Kikas V.* About the properties of glass phase of oil shale ash // *Transact. Tallinn Techn. Univ.* 1971. No. 308. P. 15–26 [in Russian, Summary in English].
23. *Kikas V., Uustalu E. et al.* Study of the composition and properties of ash fractions of oil shale burnt at Estonian Power Plant // *Report of TTU*. 1985. Tallinn, TTU [In Estonian].
24. *Õispuu L., Randmann R., Rootamm R.* Components of oil-shale ash deposited on ash-fields, consumed or ejected with exhaust gases // *Transact. Tallinn Techn. Univ.* 1994. No. 739. P. 94–114 [in Estonian, Summary in English].
25. Сборник трудов по изучению сланца-кукерсита (Studies on oil-shale (kukersite) ashes) No. 6 // *Transact. Tallinn Techn. Univ.* 1972. No. 335 [in Russian].
26. *Utsal K.* The use of the X-ray diffraction method for the complex study of the matter composition of oil shale // *Oil Shale*. 1984. Vol. 1, No. 1. P. 69–79 [in Russian, Summary in English].
27. *Vingisaar P., Kattai V., Utsal K.* The composition of the kukersite in the Baltic oil shale basin // *Proc. Estonian Acad. Sci. Geol.* 1984. Vol. 33, No. 2. P. 55–62 [in Russian, Summary in English].
28. *Pets L.* Probable modes of occurrence of elements in kukersite mineral matter // *Oil Shale*. 1998. Vol. 15, No. 3. P. 268–276 [in Russian, Summary in English].
29. *Pets L.* Probable modes of occurrence of trace elements in oil shale ashes of power plant // *Oil Shale*. 1999. Vol. 16, No. 4S. P. 464–472 [in Russian, Summary in English].
30. *Õispuu L., Randmann R., Rootamm R., Ingermann K.* The feature of oil shale burnt at Estonian power plants in 1959–1997 // *Oil Shale*. 1999. Vol. 16, No. 3. P. 273–282.

31. *Õispuu L., Rootamm R.* Environment pollution by burning pulverized oil shale // *Transact. Tallinn Techn. Univ.* 1994. No. 739. P. 79–85 [in Estonian, Summary in English].
32. *Pets L.* Depositions of macro- and microelements from atmospheric emission of oil shale ashes in northeastern Estonia // *Oil Shale.* 1997. Vol. 14, No. 2. P. 163–170 [in Russian, Summary in English].
33. *Jegorov D., Trapido M., Rajur K., Loosaar J.* Oil shale energetics and environment // *Problems of Contemporary Ecology : Abstr. 5th Conf. in Ecology (Tartu, April 24–28, 1991).* Tartu, 1991 [in Estonian, Summary in English].
34. *Arro H., Prikk A., Loosaar J.* Air pollution and oil-shale power plants // *Problems of Contemporary Ecology. Abstr. 6th Conf. in Ecology (Tartu, March 23–25, 1988).* Tartu, 1988 [in Estonian, Summary in English].
35. *Ots A.* Formation of air-polluting compounds while burning oil shale // *Oil Shale.* 1992. Vol. 9, No. 1. P. 63–75.
36. *Kallaste T., Roots O., Saar J., Saare L.* Air Pollution in Estonia 1985–1990 : *Environmental Report 3.* – Helsinki, 1992.
37. *The Quality of Atmospheric Air in Ida-Virumaa / V. Liblik, H. Kundel.* (comp. and eds.); *Publ. Inst. Ecol., Envir. Dep. of Ida-Viru County Government.* – Jõhvi, 1995 [in Estonian, Summary in English].
38. *Impact of Oil Shale Mining and Processing on the Environment in North-East Estonia / V. Liblik, J.-M. Punning* (eds.). – *Estonian Academy Publishers, Tallinn,* 1999 [in Estonian, extended summary in English].
39. *Aunela L., Häsänen E. et al.* Emissions from oil shale power plants // *Oil Shale.* 1995. Vol. 12, No. 2. P. 165–177.
40. *Hansmann K.* Bundes-Immissionsschutzgesetz und ergänzende Vorschriften. Das Deutsche Bundesrecht. Erläuterte Ausgabe. Band 8. Baden-Baden, 1991.
41. *Oil Shale.* 2000. Vol. 17, No. 2 Special: Oil Shale and the Environment.
42. *Õpik I.* The Influence of Inorganic Matter of Oil shale on the Conditions of Boiler Operation : *Dissertation.* Tallinn, 1961 [in Russian].
43. *Õpik I.* Low-temperature combustion of Estonian oil shale: theory, practice, critique // *Oil Shale.* 1985. Vol. 2, No. 3. P. 289–296 [in Russian, Summary in English].
44. *Ots A.* Corrosion and Wear of the Heating Surfaces of the Boilers. – Moscow, 1987 [in Russian].
45. *Ots A.* Utilization of the Estonian oil shale in power engineering. Problems concerning a steam boiler // *Oil Shale.* 1988. Vol. 5, No. 1. P. 1–14 [in Russian, Summary in English].
46. *Arro H., Õpik I.* Über den Einfluss von Cloriden auf die Ansatzbildung und Korrosion der Heizflächen bei der Verbrennung Estnischer Brennschiefer // *Proc. Estonian Acad. Sci. Phys. & Math.* 1967. Vol. 16, No. 4. P. 483–488.
47. *Tallermo H., Lausmaa T., Klevtsov I., Nuutre M.* The influence of chlorine in ash deposits on 12Cr1MoV alloy high-temperature corrosion // *Oil Shale.* 1997. Vol. 14, No. 3. P. 307–316.
48. *Tallermo H., Tomann E., Klevtsov I., Bojarinova T., Nuutre M.* Corrosion resistance of ferritic alloys 13CrMo44 10CrMo910 in conditions of superheaters of pulverised oil shale boiler // *Oil Shale.* 1997. Vol. 14, No. 3. P. 317–327.

49. Kikas V. Mineral matter of kukersite oil shale and its utilization // Oil Shale. 1988. Vol. 5, No. 1. P. 15–28 [in Russian, Summary in English].
50. Öpik I. Ash utilization after combustion and thermal processing of Estonian (kukersite) oil shale // Oil Shale. 1989. Vol. 6, No. 3. P. 270–275.
51. Kikas W. Composition and binder properties of Estonian kukersite oil shale ash // Zement-Kalk-Gips International. 1997. Vol. 50, No. 2. P. 112–126.
52. Turbas E. Use of oil shale ashes as a lime fertilizer in Estonian // Oil Shale. 1992. Vol. 9, No. 4. P. 301–309 [in Russian, Summary in English].
53. Kaljuvee T., Trikkel A., Kuusik R. Reactivity of oil shale ashes towards sulfur oxide. 1. Activation of high-temperature ashes // Oil Shale. 1997. Vol. 14, No. 3. P. 393–407.
54. Kuusik R., Kaljuvee T., Veskimäe H., Roundygin Yu., Keltman A. Reactivity of oil shale ashes towards sulfur oxide. 3. Recurrent use of ash for flue gas purification // Oil Shale. 1999. Vol. 16, No. 4. P. 303–314.

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The paper is devoted to dramatic events, which affected science and research, particularly the people of science in the Estonian Republic during a fifty-year period (1940–1991) of its history. The main attention is devoted to the period 1940–1945, when critical changes in the research system, including a systematic extermination of the local intelligentsia took place.

Introduction

This paper is devoted to dramatic events that affected a fifty-year period (1940–1991) of Estonian science and research, with particular attention to how these events affected the people and structure of science. This period saw three waves of occupation, a great war raged over the small country, and there were fundamental alterations in the political, social and economic structures, and environment. Many of the specifics of science and research development in Estonia and the other two Baltic States were determined by these historical events – by the radical changes that took place in the region. This illustrates a principal difference between science in the Baltic States and in most of the rest of Europe since the 17th century: the evolution of science in the Baltic States has been dictated to a great extent by the political and economical interests of those foreign powers that ruled the region.

In this paper the main focus is on the 1940's and 1950's when there were major changes in the R&D-system, including a systematic extermination of the local intelligentsia. We will point out only a few of the most drastic features of these years.

Estonia provides a unique example of the only country in Europe where (over the last four centuries) the science establishment has undergone five cycles of rapid collapse and subsequent new beginnings. With every collapse