Study of Thermooxidation of Oil Shale Samples and Basics of Processes for Utilization of Oil Shale Ashes

Tiit Kaljuvee 1*, Mai Uibu 1, Can Rüstü Yörük 1, Marve Einard 1, Andres Trikkel 1, Rein Kuusik 1, Olev Trass 2, Igor Štubňa 3, Tomáš Húlan 3, Valli Loide 4 and Jekaterina Jefimova 5

1 Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia; mai.uibu@taltech.ee (M.U.); can.yoruk@taltech.ee (C.R.Y.); marve.einard@taltech.ee (M.E.); andres.trikkel@taltech.ee (A.T.); rein.kuusik@taltech.ee (R.K.)
2 Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON M5S 3E5, Canada; olev.trass@utoronto.ca
3 Department of Physics, Constantine the Philosopher University, A. Hlinku 1, 949 01 Nitra, Slovakia; istubna@ukf.sk (I.Š.); thulan@ukf.sk (T.H.)
4 Department of Agrotechnology, Estonian Crop Research Institute, J. Aamisepa 1, 48309 Jõgeva, Estonia; valli.loide@gmail.com
5 Estonian Marine Institute, University of Tartu, Mäealuse tee 14, 12618 Tallinn, Estonia; jekaterina.jefimova@hotmail.com
* Correspondence: tiit.kaljuvee@taltech.ee

Abstract: A circular economy becomes an object of actual discussions as a real alternative to the existing linear economy system. The problem is actually in Estonia also, first of all in the sector of heat and power production which based mainly on the combustion of local solid fossil fuel—Estonian oil shale (OS) resulting in the formation of ~5–6 million tons of OS ashes annually. The thermooxidative decomposition of OS samples from different deposits and estimation of the possibilities of utilization of OS ashes formed at both—pulverized firing (PF) and circulating fluidized bed combustion (CFBC) of Estonian OS were studied. The thermal analysis combined with evolved gas analysis (EGA) methods like Fourier transform infrared (FTIR) and mass-spectroscopy (MS) was exploited. It was established that the differences in the thermal behaviour of different OS samples are caused by the differences in the chemical matrix of organic matter, chemical and mineralogical composition of the inorganic part of OS, and morphology of samples. It was also found that moderate grinding of OS ashes with simultaneous moderate water treatment notably improved the SO2 binding efficiency of cyclone ash, and that the strength and leachability characteristics of granulated OS ashes strongly depend on the post-granulation treatment conditions allowing to increase the soil neutralizing ability of the granulated products. This overview was based on our investigations carried out during the last fifteen years.

Keywords: ceramics; granulation; oil shale/ash; SO2 capture; TG-DTA-FTIR/MS; thermooxidative decomposition

1. Introduction

Over the last decade, increasing attention was paid to the circular economy as an alternative to the existing linear economy system which is based on continuous growth and increasing resource throughput [1–6]. The importance of re-use of wastes and utilization of by-products has been realized. There is also a new strategic interest in Estonia, especially in the heat and power production industry. Approximately 70% of the energy production in Estonia is based on the combustion of Estonian OS containing organic matter on the level of only 30–35%. The inorganic part of OS consists mostly of carbonates and sandy-clay minerals. The sulfur content is around 1.5%. Around 10 million tons of OS was used in heat and power production and ~5–6 million tons of OS ashes was formed in...
Estonia in 2019. OS ashes can be used in cement production, road building, agriculture, etc. However, the level of utilization of these ashes is poor—only ~2.5% of the total amount of OS ashes is used, and the other part is left unused and landfilled.

A number of changes have occurred in Estonia’s OS-based energy sector. On the one hand, the implementation of circulating fluidized bed combustion (CFBC) boilers has improved fuel efficiency and lowered greenhouse gas emissions. There are also some pulverized firing (PF) boilers in partial exploitation. On the other hand, the changes in process conditions, in particular, the lowering of the temperature from 1200–1400 °C (used in PF) to 750–800 °C (used in CFBC), have not affected only the physical and chemical characteristics of the OS ashes [7] but could also affect the composition of formed and evolved gaseous compounds.

The TG-DTA technique combined with evolved gas analysis methods is a widespread tool for studying high-temperature processes occurring at the thermal treatment of solid fossil fuels in different gaseous [8–17] atmospheres.

Comparing oil shales with another solid fossil fuel-coal-oil shale samples are characterized by a higher content of inorganic matter—on the level of 70–80% [14–16], and coal samples, except lignite type of coal, are usually on the level of 5–30% [10,12,13,17]. Considering the very complicated composition of organic matter (kerogen) in Estonian oil shale [18], it could be exploited, in addition to energy production, for the production of much larger nomenclature of organic compounds—as aliphatic as well as aromatic ones—which is not the case with coal.

Different transformations take place within the inorganic part of OS during the combustion process using either PF or CFBC technology. A part of free Ca, Mg-oxides formed remains in ashes as free oxides, but another part actively participates in the formation of different silicates with varying compositions [7].

In the case of PF of solid fossil fuels, one serious problem is the contamination of the atmosphere (in addition to carbon dioxide which is common in CFBC also) with sulphur dioxide. Fly ashes formed in coal combustion with or without different additives like lime, hydrated lime, and more, have been tested as suitable sorbents for SO₂ binding into the solid phase [19–24].

The possibilities to use a Szego Mill™ for reactivation of coal combustion ashes from FBC units with the addition of limestone has been studied in [25,26]. Good results were obtained with moderate grinding of ashes with the simultaneous adding water on the level of eight percent only being at that in the range of semidry grinding [26]. The reactivity of ashes formed at PF and at CFBC of Estonian OS toward CO₂ and SO₂ binding with clarifying the binding mechanism has been presented in our earlier publications [27–30]. Additionally, the possibilities of using the Szego Mill™ at the activation of fly ash for SO₂ binding and comparing it with commercial lime used in the Alstom semi-dry DeSO₂ system at the Eesti Power Plant was studied [31].

One of the most serious global problems, especially considering the world’s increasing population, is the acidification of agricultural soils which is caused by the precipitation from the atmosphere of acidifying gases (SO₂, NH₃, HNO₃, etc.), application of acidifying fertilizes (urea, ammonium salts, etc.), mineralization of organic matter, nutrient uptake by crops, leaching processes in soil, etc.

In Estonia, the evaporation is about 250–300 mm lower than the annual average rainfall which causes the leaching of Ca,Mg-compounds from the soil under the influence of soil filtrating water, and as a result, the soil becomes acidic and less fertile [32,33].

Different ashes (MWI, coal) and blends based on these ashes with different additives (lime, gypsum, etc.) have been studied in neutralizing acidic soils [34–41]. As fine materials are characterized by quick leaching in acidic environments, then such kinds of materials have only limited neutralizing effects in acidic soils [32]. For prolongation of the soil neutralizing ability, powder-like materials in agriculture and forestry are granulated before use [26,37,42,43].
The possibilities of utilization of different ashes in ceramic and glass-ceramic industries replacing a part of clay with ash additives are also intensively studied [44–53]. Both areas could be suitable for the utilization of OS ashes also [54–56].

In this paper, the overview of the results of our long-term investigations obtained by studying the phenomena and transformations by implementing thermal analysis techniques for the following processes is presented:

- thermooxidative decomposition characteristics of OS samples from different deposits with simultaneous gas phase analysis,
- potential of SO₂ uptake by different OS ashes formed at PF and CFBC of Estonian OS with clarifying the effect of pre-treatment of ashes (grinding, hydration) on SO₂ binding,
- influence of post-granulation treatment on the physico-mechanical and physico-chemical characteristics of granulated OS ashes with aim of using them for neutralizing acidic soils,
- influence of OS ash additives on the thermal behaviour of blends based on Estonian clays.

2. Materials and Methods

2.1. Methods

The experiments with a Setaram Setsys1750 thermoanalyzer (Setaram Instrumentation, Caluire, France) coupled with Nicolet 380 Spectrometer (Thermo Fisher Scientific, Madison, USA) (3.1) or Setaram Labsys Evo 1600 thermoanalyzer (Setaram Instrumentation, Caluire, France) coupled with Pfeiffer OmniStar Mass Spectrometer (Pfeiffer Vacuum Technology AG, Asslar, Germany) (3.3 and 3.4) by a heated transfer line were carried out under non-isothermal conditions by heating up to 1050 °C at the heating rates of 1, 2, 5, 10 and 50 °C per min in a gaseous atmosphere containing 21% of O₂ and 79% of Ar. Standard 100 µL Pt or alumina crucibles were used, the mass of the samples was 12 ± 0.5 mg and the gas flow was 60 mL min⁻¹.

XRF and XRD analysis was performed with Bruker S4 Pioneer and Bruker D8 Advanced diffractometers (Bruker Corporation, Karlsruhe, Germany), respectively. For XRD analysis was used Ni-filtered CuKα radiation collecting data in the range of 2θ from 10 to 60°. The quantitative mineral composition was determined by full-profile Rietveld analysis using the Siroquant™ V4 software system [57,58].

FTIR analysis was performed with Bruker ALPHA (Bruker Corporation, Karlsruhe, Germany). The surface observations were carried out with the scanning electron microscope Jeol JMS-8404A (Joel Ltd., Tokyo, Japan), BET specific surface area (SSA) and porosity measurements with Sorptometer Kelvin 1042 (Costech International SRL, Pioltello, Italy) and the particle size distribution was measured on the analyser Partica LA-950V2 (Horiba LTD., Kyoto, Japan).

The content of total carbon and total inorganic carbon were determined with an Eltra CS S80 (Haan, Germany) and the content of free CaO using the ethylene glycol method.

2.2. Thermooxidative Decomposition of Oil Shale Samples

2.2.1. Methods

The gross calorific (high heating) value and element analyses of samples were determined using calorimeter C2000 (IKA—Werke GmbH, Staufen, Germany), and Vario EL Element Analyzer (Analysensysteme GmbH, Langenselbold, Germany), respectively.

The content of organic matter and fixed carbon (X) in the dry samples was calculated by the next formula:

\[ X = [100 - A_d - (CO_2)_{xe} \] \%

where \( A_d \) is the content of ash, %; \( (CO_2)_{xe} \) is the content of mineral carbon dioxide, %, both on dry bases.
2.2.2. Materials

The thermooxidative decomposition of two samples of Estonian OS, one sample of Jordanian, Israel and Moroccan OS and one sample of Estonian OS semicoke (SC) formed in the production of shale oil at thermal processing of Estonian OS [15,16,59] have been studied.

2.2.3. Material Characterization

The content of organic matter and fixed carbon in OS samples was between 17–30%, except in EOSII where the content of it was much higher—63% and in semicoke much lower—13.1% (Table 1). The content of mineral CO2 indicated the high content of carbonates—calcite, dolomite. Sulphur was presented as pyritic, organic and sulphate sulphur, and in semicoke, additionally, sulhide sulphur. The content of hydrogen in OS samples varied in a large range—from 1.5% (IOS) to 6.0% (EOSII), and in semicoke it was 1.2%. There were significant differences observed in the mole ratio of (H/C)total for OS (between 1.02 and 1.47), in semicoke, it was much lower—0.81 (Table 1). The higher mole ratio of (H/C)total is the indicator for the more probable formation of volatile organic compounds at thermooxidative decomposition of studied samples.

Table 1. Main characteristics of sample (on dry bases).

| Content, %     | EOS I | EOS II | JOS | IOS | MOS | SC    |
|----------------|-------|--------|-----|-----|-----|-------|
| Organic matter + fixed C | 29.7  | 63.1  | 22.6 | 17.1 | 18.5 | 13.1  |
| Ash            | 50.5  | 32.1  | 61.9 | 60.3 | 66.4 | 68.8  |
| (CO2)tot       | 19.8  | 5.8   | 15.5 | 22.6 | 15.1 | 18.1  |
| Srot           | 1.63  | 1.22  | 3.52 | 2.60 | 1.97 | 2.38  |
| Spyr           | 1.20  | 0.47  | 0.28 | 0.88 | 0.34 | 0.60  |
| Ssulph         | 0.10  | 0.04  | 0.12 | 0.32 | 0.10 | 0.44  |
| Sorg           | 0.33  | 0.71  | 3.12 | 1.40 | 1.53 | 0.74  |
| Sulphide       |       |       |     |     |     | 0.60  |
| N              | 0.53  | 0.09  | 0.42 | 0.39 | 0.50 | 0.52  |
| H              | 3.00  | 5.96  | 2.24 | 1.46 | 1.65 | 1.21  |
| C              | 28.3  | 48.5  | 22.2 | 17.1 | 16.5 | 17.9  |
| (H/C) mole total | 1.27 | 1.47  | 1.21 | 1.02 | 1.21 | 0.81  |
| Gross calorific value, MJ/kg | 10.24 | 22.43 | 8.14 | 4.90 | 6.11 | 4.12  |

2.3. Oil Shale Cyclone Ash in the Binding of Sulphur Dioxide

2.3.1. Materials

To obtain more effective sulphur dioxide binding from flue gases at PF of Estonian OS the Alstom semidry DeSOX (Novel Integrated Desulphurization, NID) system based on the use of commercial lime was installed a few years earlier at the Eesti Power Plant. Considering that the content of free CaO in cyclon ash formed is on the level of 20–25%, the possibility of replacing expensive lime with activated cyclon ash was studied.

2.3.2. Material Characterization

The initial cyclone ash contained: CaOtot—57.2%, CaOfree—26.3%, MgO—2.0%, SiO2—23.8, CO2—1.7%, Srot—1.53%, LOI—3.4%. The main mineral phases in the initial cyclone ash were lime, merwinite, belite, periclase, anhydride, melilit, illite-smectite, quartz, etc. The content of free CaO in the commercial lime was 77.4% [31]. For activation of cyclon ash the Szego Mill was used. Initial cyclone ash, dry ground and semi-dry ground ash with 5% mass and 7% mass water added at grinding, commercial lime from Eesti Power Plant and beforehand hydrated lime as sorbents for SO2 binding were tested.

2.3.3. Method
The temperatures of the experiments in the Setaram Labsys thermoanalyzer were 80, 300, 400, 500 and 700 °C. In the beginning, the furnace was heated up to the test temperature at a heating rate of 20 °C min⁻¹ and stabilized for 20 min. Then, the model gaseous mixture contained 1 mol% SO₂ in nitrogen was led to the reaction chamber with a flow rate of 20 mL min⁻¹ for 45 min. A Pt-multiplate crucible was used and the mass of studied samples was 80 ± 0.5 mg [31].

Three parameters were calculated to characterize the extent of gas–solid interactions: SO₂- binding capacity (BC; mg SO₂ bound by 100 mg of sample), SO₂- binding rate (W; mg SO₂ per mg sample min⁻¹), SO₂-binding efficiency, (BE, %) showing the extent of utilization of free CaO contained in the sample.

### 2.4. Influence of Post-Granulation Treatment of Oil Shale Ashes

One large-scale possibility for utilization of alkali OS ashes is the use of them in the liming of acidic soils. For minimizing the possible negative influence on soils at liming the OS ashes should be granulated. Granulation of ashes enables also modification of the composition of the granulated product via adding different nutrients and microelements need for normal growth of different plants. To improve the physico-mechanical and physico-chemical characteristics of granulated products, different post-granulation treatment methods were used, and for estimation of differences in these characteristics of differently treated samples thermal analysis was exploited.

#### 2.4.1. Materials

The ashes studied were electrostatic precipitation ash (ESPA) from CFBC and cyclon ash from PF boilers from the Eesti Power Plant [60,61]. Clay from AS Kunda Nordic Cement factory (Kunda, Estonia) was used as the solid binding modifier to improve the physical and mechanical characteristics of granulated products. Without clay additives, the OS ashes studied granulated badly.

#### 2.4.2. Material Characterization

The content of CaO was 38.3% and 51.6%, free CaO 9.5% and 20.9%, MgO 4.4% and 4.9%, sulphur 2.3% and 2.0%, SiO₂ = 33.8% and 24.5%, respectively, in ESPA and cyclon ash. The main mineral phases in the ashes were lime, quartz, calcite, anhydrite, periclase, and different silicates like illite–smectite, orthoclase, belite, melilite, merwinite, and more. The mean particle size was 32.5 and 55.8 µm, the SSA 3.69 and 0.91 m²g⁻¹, and the porosity 5.94 and 1.67 mm³g⁻¹, respectively, for ESPA and cyclon ash. Particles of ESPA was characterized by an irregular shape and porous surface, but particles of cyclon ash, formed at much higher temperatures were, especially smaller ones, with a regular round shape and smooth surface [60].

The content of CaO in clay was 0.78%, SiO₂ 58.7%, Fe₂O₃ 6.8%, Al₂O₃ 17.7%, K₂O 6.2%, sulphur 0.28% and MgO 2.5%. The main mineral phases in clay were illite–smectite (50.6%), quartz (25.6%), orthoclase (5.3%), and chlorite (12.5%). SSA for clay was 40.53 m²g⁻¹, porosity 59.95 mm³g⁻¹ and mean particle size 15 µm [61].

#### 2.4.3. Method

**Granulation of Ashes**

Granulation of ashes was carried out on a plate granulator with a diameter of 0.55 m or 1.4 m using re-cycling ash transportation water from Eesti Power Plant, “black liquor” (15%) from Horizon Pulp&Paper Ltd. (Kehra, Estonia) as well as water–glass (15%), polycrylamide (1%) aqueous solutions, etc., as the binding agents [60,61], more precisely with transportation water. At first, the homogeneous mixture of ash and clay was performed which was then gradually added to the disc using a vibrofeeder at the same time
with a liquid binder. For improving the compressive strength of granules, different storing/drying regimes were tested: immediate drying after granulation at 105 °C or at 60 °C, stored hermetically closed before drying, stored/dried in the open air at room temperature, stored in the atmosphere of carbon dioxide with a higher content of CO₂ (15%, similar to flue gases at Eesti Power Plant) before drying [60,61].

Experiments were focused on three important parameters that are mostly considered in the case of fertilizers–particle size, compressive strength and leachability of components. For comparing the leachability of components the granulated, as well as non-granulated OS ashes, were tested using for that laboratory lysimeters.

**Lysimetric Test of Samples**

At lysimetric test the granulated, and for comparison, the origin ashes were mixed in the upper part (1/3 level) of Gleyic Podzoluvisol soil (pH = 4.7) with the stoutness of 0.25 m. The mass of ashes was calculated on the level of 7.5 t CaCO₃ ha⁻¹ considering the content of calcium in the studied ashes. The content of moisture in the soil during the lysimetric tests was held on the level of 40–50% considering the saturation ability of soil with moisture. The filtrates were collected on the 2nd, 4th and 21st week after starting the test, and solutions were analyzed for Ca²⁺, Mg²⁺ and K⁺ content using atomic absorption spectrophotometer Spectra AA (Varian Inc., Mulgrave, Australia) and SO₄²⁻ content using spectrophotometer SpectroDirect (The Tintometer Ldt., Dortmund, Germany) Before and after the test the soil was analyzed on the content of available calcium, magnesium, potassium in Mehlich 3 extract [62], water-soluble sulphate ion and pH value were also determined.

**2.5. Influence of OS Ash Additives on the Thermal Behaviour of Blends Based on Estonian Clays**

**2.5.1. Materials**

The influence of different OS ashes formed, respectively, at PF (cyclon ash and DeSOx ash, Eesti Power Plant) and at CFBC combustion (ESPA, Eesti and Auvere Power Plants) of Estonian OS at electricity production on the thermal behaviour of Estonian clays from Kunda and Arumetsa deposit, and, for comparison, on the illitic clay from Füzérradvány (Hungary) has been studied [55,56,63].

**2.5.2. Material Characterization**

Clay samples studied contain a high level of illite + illite–smectite + mica and quartz: in Kunda clay 51.1% and 27.2%, in Arumetsa clay 48.9% and 18.5%, and in illitic clay 52.9% and 17.5%, respectively. In addition, kaolin, orthoclase and calcite in both, Kunda and Arumetsa clay, gypsum and pyrite only in Kunda clay, plagioclase and dolomite in Arumetsa clay, and mica and adularia in illitic clay are also contained [55,56]. The content of organic carbon in Arumetsa and Kunda clay is much higher—0.32 and 0.21%, respectively, as compared to Kunda clay, is characterized by higher SSA—44.71 and 30.86 m²g⁻¹, porosity—77.63 and 51.87 mm³g⁻¹, and smaller mean particle size—12.7 and 15.1 µm, respectively. The SSA and porosity for illitic clay were 48.79 m²g⁻¹ and 82.14 mm³g⁻¹, respectively, and the mean particle size 17.3 µm (Table 2).

**Table 2. Chemical composition (%) and some physical characteristics of initial samples.**

| Item Samples | CaO total | CaO free | MgO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₄ total | K₂O | Na₂O | LOI | Crc/Crct | Corg⁻¹ | BET SSA, m²g⁻¹ | Porosity, mm³g⁻¹ | dmean µm |
|--------------|-----------|----------|-----|------|-------|-------|-----------|-----|------|-----|--------|---------|----------------|-------------------|---------|
| Arumetsa clay | 1.5       | 2.7      | 65.5 | 18.4 | 6.8   | 0.08  | 4.5       | 0.58| 6.9  | 0.39/0.07 | 0.32 | 44.71 | 77.63 | 12.7       |
| Kunda clay   | 0.4       | 2.3      | 61.4 | 17.8 | 5.9   | 1.68  | 6.0       | 0.08| 4.8  | 0.23/0.02 | 0.21 | 30.86 | 51.87 | 15.1       |
| Illitic clay | 0.3       | 1.2      | 57.0 | 25.0 | 1.9   | 0.08  | 8.5       | 0.02| 7.0  | 0.06/0.09 | 0.14 | 48.79 | 82.14 | 17.3       |
| CFBC/ESPA    | 30.7      | 9.0      | 4.5  | 34.4 | 8.6   | 4.2   | 4.4       | 0.19| 5.6  | 1.13/1.13 | 3.67 | 5.94  | 32.5  |           |
| PF/CA        | 51.6      | 22.7     | 4.9  | 24.5 | 6.4   | 3.9   | 3.4       | 2.0 | 0.14 | 1.5        | 0.91 | 1.69  | 55.8  |           |
| PF/DeSOx | 36.3 | 7.9 | 4.7 | 28.5 | 7.3 | 3.6 | 9.3 | 3.6 | 0.32 | 6.7 | 1.01/1.01 | 1.43 | 3.84 | 49.6 |
| CFBC/Auve re FA | 37.3 | 12.0 | 2.4 | 24.0 | 11.0 | 5.4 | 3.6 | 3.9 | 0.11 | 9.4 | 1.45/1.38 | 0.07 | 4.75 | 8.93 | 42.0 |

\[^{\circ}\text{C}_{\text{org}} = \text{C}_{\text{TC-CTIC}}; \quad \text{C}_{\text{TC-}}\text{total carbon, } \text{C}_{\text{CTIC-}}\text{total inorganic carbon.}\]

The ashes differ in their chemical compositions (CaO free between 9.0% and 22.7%, MgO: 2.4% and 4.9%, CaO: 30.7% and 51.6%, SO₃: 3.4% and 9.3%, SiO₂: 24.0% and 34.4%) as well as their mineralogical and grain-size compositions. The OS ashes are highly reactive (alkaline), for example, the content of free CaO in cyclon ash is 22.7% and in Auvere fly ash 12.0%, respectively (Table 2). The mean particle size varied between 32.5 and 55.8 \(\mu\)m being smaller for ESPA ash. The BET SSA varied between 0.91 and 4.75 m²g⁻¹, and the porosity between 1.69 and 8.93 mm³g⁻¹, at that bigger values, are characteristic of Auvere ash (Table 2). Particles of ESPA ashes are characterized by irregular shape and uneven surface, but particles of pulverized firing ashes with their regular round shape and smooth surface [55,63].

The composition of clay with 40% of previously fired at 1050 °C clay (grog) was used as a basement one. In the blends studied the fired clay was replaced with OS ash additives.

2.5.3. Methods

The experiments were carried out under non-isothermal conditions using Setaram Labsys Evo 1600 thermoanalyzer coupled with Pfeiffer OmniStar Mass Spectrometer by a heated transfer line (more precisely in Section 2.1.).

3. Results and Discussion

3.1. Thermooxidative Decomposition of Oil Shale Samples

3.1.1. Thermal Analyses

The thermooxidative decomposition of OS and semicoke samples studied proceeded in three stages, but depending on the origin of OS and the heating rate used, certain differences in the thermal behaviour of samples were observed. For example, at the heating rates 1 °C and 5° per min, the thermooxidation of the lighter, more volatile part of organic matter (kerogen) (sub-step IA) lasted up to 354 °C and 397 °C, respectively, and at the heating rate of 50 °C per min—up to 491 °C (Figure 1). Thermooxidation of the heavier part of organic matter (sub-step IB) and thermooxidation of pyrite contained in OS samples continues at the heating rates 1 °C and 5 °C per min up to 460 °C and 510 °C, respectively. The third stage (step II) was mainly the decomposition of carbonates, and lasted up to 720 °C and 800 °C, respectively, at the heating rates of 1 °C and 5 °C per min (Figure 1). The total mass loss at lower heating rates considering both steps of thermooxidation for studied samples was between 31% and 67%, the highest for EOSII and the smallest for SC.
Figure 1. Thermoanalytical curves of Estonian OS I. at different heating rates.

At the heating rate of 50 °C per min, it was not possible to fix the boundary between the first and second steps in the DTA curve because the decomposition of carbonates started before the thermooxidation of a heavier part of organic matter was completed (Figure 1). The total mass loss for OS samples heating up to 900 °C was 4–5% and for semicoke 3.1% smaller than at low heating rates. This indicates that a part of acidic gaseous species like SO₂, CO₂, HCl formed at thermooxidative decomposition of the samples is bound into the solid by free Ca, Mg-oxides formed at the decomposition of carbonates and by primary or/and secondary silicates [27–29,64,65].

Depending on the heating rate and on the origin of the OS sample, the boundary between the substeps IA and IB is better or worse fixed (Figure 2). EOS I and EOSII as well as for JOS are better differentiated than IOS, MOS and semicoke samples which is caused by the higher content of volatile compounds in kerogen (higher H/C mole ratio) like in Estonian and Jordanian OS samples (Table 1).
3.1.2. FTIR Analysis

Table 3 presents the list of gaseous compounds formed and emitted during the thermo-oxidative decomposition of studied samples varying slightly in composition but more in the intensities of characteristic profiles of these compounds.

| Name                        | Wavenumber/cm\(^{-1}\)                                                                 |
|-----------------------------|----------------------------------------------------------------------------------------|
| H\(_2\)O                    | 3900–3500, 1900–1200                                                                 |
| CO\(_2\)                    | 2400–2250, 2380, 678                                                                  |
| CO                          | 2250–2050, 2177, 2114                                                                  |
| HCl                         | 3000–2700                                                                              |
| NH\(_3\)                    | 967, 932                                                                               |
| COS                         | 2075, 2053                                                                             |
| HCN                         | 713                                                                                    |
| methane                     | 3017, 1307                                                                             |
| ethane                      | 2970, 1457                                                                             |
| ethylene                    | 2650, 950                                                                             |
| methanol                    | 1060, 1035, 1008                                                                       |
| ethanol                     | 1244, 1052                                                                             |
| p-xylene                    | 1512, 793                                                                             |
| chlorobenzene               | 1474, 742                                                                             |
| C-H stretching vibration    | 3100–2700 (adjacent to double bonds, aromatic rings; aliphatic hydrocarbons)          |
| C=O stretching vibration    | 1850–1600 (ketone, acid, aldehyde)                                                     |
| C=C stretching vibration    | 1600–1450 (aromatic compounds)                                                         |
| C-H bending vibration       | 1500–1300 (saturated aliphatic hydrocarbons)                                           |

The most intensive absorption bands in FTIR spectra are characterized by the emission of water (broad band in the range of 1900–1300 cm\(^{-1}\)) and carbon dioxide (maximums...
at 2380 and 678 cm\(^{-1}\)). Formation and emission of form- (1749 and 1177 cm\(^{-1}\)) and acetaldehyde (1763 and 1419 cm\(^{-1}\)), formic (1749 and 1107 cm\(^{-1}\)) and acetic (1798 and 1177 cm\(^{-1}\)) acids, ketons (1710–1720 cm\(^{-1}\)), sulphur dioxide (1376 and 1361 cm\(^{-1}\)), methane (3018 and 1307 cm\(^{-1}\)), ethane (2970 and 1457 cm\(^{-1}\)) and chlorobenzene (1474 and 742 cm\(^{-1}\)) were clearly fixed at thermooxidative decomposition for all samples studied (Figure 3a,b). The other compounds formed and emitted at thermooxidative decomposition like ethylene (1648 and 950 cm\(^{-1}\)), methanol (1034 and 1008 cm\(^{-1}\)), ethanol (1244 and 1052 cm\(^{-1}\)), COS (2074 and 2052 cm\(^{-1}\)), p-xylene (1512 and 793 cm\(^{-1}\)), NH\(_3\) (967 and 933 cm\(^{-1}\)) in FTIR spectra of EOS and JOS are fixed with fewer intensities. Absorption bands characteristic to ethylene, methanol and ethanol at thermooxidative decomposition of MOS (Figure 3b) and IOS, and ethylene, COS, p-xylene and methane at thermooxidative decomposition of SC were fixed in FTIR spectra on the level of traces only. The absorption bands characteristic to methanol and ethanol at thermooxidative decomposition of SC, and to NH\(_3\) at thermooxidative decomposition of MOS were missing in FTIR spectra [15]. Missing and/or much poorer level emission of gaseous compounds formed at thermooxidative decomposition of studied samples is caused, first of all by the poorer content of volatile organic matter in IOS, MOS and semicoke compared with EOS and JOS (Table 1).

At lower heating rates (5 °C and 10 °C per min), the emission of many gaseous compounds formed at thermooxidative decomposition of studied samples started at 190–250 °C (Figure 4a), but the others—more complicated compounds like chlorobenzene and p-xylene—started at temperatures of 250–300 °C (Figure 4b). At the higher heating rate—50 °C per min—for the most gaseous compounds emitted, the starting point was moved 50–60 °C towards higher temperatures with the simultaneous increase in intensities of most of the species in FTIR spectra (Figure 5a,b). This is caused by the shortening of the contact-
time between organic gaseous compounds formed at thermodo-oxidative decomposition and oxygen unable for complete oxidation of these species before leaving the furnace [16].

**Figure 4.** Emission profiles of methane (3014 cm\(^{-1}\)) (a) and chlorobenzene (742 cm\(^{-1}\)); (b) emitted in the thermooxidative decomposition of oil shale samples (10 °C min\(^{-1}\)).
So, the results obtained by using the TA technique coupled with FTIR indicated that the thermooxidative decomposition of OS has a multi-step mechanism. The differences in the thermal behavior of different OS and SC samples are caused by the differences in the chemical matrix of organic matter, chemical and mineralogical composition of inorganic matter, morphology of samples, character of chemical and physical bonds between organic and inorganic matter. The presence of minerals (high content of inorganic compounds) can restrain and postpone the formation and emission of many gaseous compounds during the thermal treatment of OS.

3.2. Oil Shale Cyclone Ash in the Binding of Sulphur Dioxide

The extensive use of fossil fuels in the power industry is a serious source of pollution of the atmosphere with different harmful gaseous compounds like SO₂, CO₂, NOₓ, and more. Considering the high content of free CaO in OS ashes formed at energy production, OS ashes—especially cyclone ash—have a great potential in the binding of acidic gaseous compounds from flue gases.

Experiments on the TG Equipment

The increase in the experimental temperature from 80 °C up to 700 °C corresponds with the increase in the SO₂ binding ability of the samples studied (Figure 6). At any studied temperature, the SO₂ binding capacity of initial OS ash was the poorest increasing from 0.26 mg at 80 °C (Figure 6a) up to 1.6 mg at 300 °C (Figure 6b) and 7.8 mg SO₂ per 100 mg of samples at 700 °C (Figure 6c) after 45 min contact between gaseous and solid phases. OS ash ground with 7% of water bound at 700 °C after 45 min contacts almost 12 mg, initial and previously hydrated lime 17.8 and 20.1 mg SO₂ per 100 mg of sample. However, considering the content of free CaO in samples, one can follow that the SO₂ binding efficiency of initial ash or the step of utilization of free CaO containing in ash is after 45 min contact on the level of 26%, of activated ash with 7% of the water on the level of 42%, but of hydrated lime only 24% (Figure 7).
Figure 6. Dependence of \( \text{SO}_2 \) binding capacity (mg \( \text{SO}_2 \) per 100 mg of sample) of sorbents on contact time between solid and gaseous phases at 80 °C (a), 300 °C (b) and 700 °C (c).

Figure 7. \( \text{SO}_2 \) binding efficiency of sorbents at 700 °C calculated on the content-free CaO bound (%).

The degree of utilization of free CaO containing in samples over the complete temperature range is presented in Figure 8. It is interesting to follow the results for lime, which are quite different from the ash data. At 300 °C, the hydrated lime bound \( \text{SO}_2 \) twice as well as the best, with 7% of water-activated ash. At higher temperatures, things reverse, and at
350–400 °C, hydrated lime, as well as semi-dry ground ashes, bound SO2 on an equal level. At 700 °C, even the untreated original ash performs better than the hydrated lime and with 7% of water-activated ash adsorbed almost twice as much as does the hydrated lime. This phenomenon is the result of breaking the sulphate shell surrounding the original ash particles with simultaneous formation of Ca(OH)2 at semi-dry grinding of ashes resulting in a larger pore volume and higher activity towards SO2 binding into the solid [31].

Figure 8. SO2 binding efficiency of sorbents calculated on the content of free CaO bound (%) after 45 min contact between solid and gaseous phases at different temperatures.

3.3. Influence of Post-Granulation Treatment of Oil Shale Ashes

It was possible to produce granules with the following characteristics: 85% had a diameter of 1–5 mm, 70–75% diameter of 1–3 mm [60,61]. This is an appropriate granulometry for exploiting the ordinary sowing machines for spreading granulated products into the field. Granules with a diameter smaller than 1 mm can be used again as seed granules and granules with a diameter over 5 mm can be crushed and recycled to reduce production losses.

3.3.1. Compressive Strength of Granules

To study more precisely the influence of carbon dioxide on the granules strength and leaching characteristics of ash components, green granules were kept in an atmosphere containing 15% of CO2 before drying [60,61]. Transportation water as an economically more suitable liquid binder was used at granulation of ashes studied.

Free CaO contained in ashes reacts during granulation and post-granulation treatment of ashes with water by the following reaction:

$$\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2$$ (2)
In the subsequent storing of green granules in the atmosphere containing carbon dioxide, the formation of calcium carbonate takes place causing the increase in the final strength of granulated product:

$$\text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O}$$

(3)

Additionally, the last process is supported by the beginning of the formation of hydrosilicates—bridges between ash particles inside granules. These processes occur more intensively with ESPA particles which are characterized by smaller size and irregular shape comparing with cyclon ash. It influences the compressive strength of ESPA granules positively: the same level of compressive strength was obtained after a shorter time comparing with these obtained by granules based on cyclon ash (CA) (Figure 9) [61].

![Figure 9. Compressive strength of granules (3–4 mm) with 10% of clay granulated with transportation water and stored in the atmosphere contained 15% of CO2.](image)

When heating up to 360 °C, the mass loss of granules was 1.9% and 1.1%, and in the temperature interval between 360–470 °C—characteristic of the decomposition of calcium hydroxide—it was 2.5% and 1.8%, respectively, for granules dried in air at 60 °C for 24h and for these stored before drying 24 h in the atmosphere containing 15% of carbon dioxide. Contrary, at temperatures between 500–800 °C—characteristic of decomposition of carbonates—the increase in the mass loss from 3.7% at storing–drying granules at 60 °C up to 5.6% at storing granules 24 h in the atmosphere with a high content of carbon dioxide took place. The influence of storing–drying conditions of green granules on the thermal behaviour of differently treated samples is well followed by DTG curves (Figure 10a) and emission profiles of H2O and CO2 obtained by MS analysis of evolved gases (Figure 10b).
Figure 10. DTG curves (a) and emission profiles of H₂O and CO₂ (b) for cyclone ash +10% clay granulated with transportation water (heating rate 10° min⁻¹).

In addition, in Figure 11a, the influence of post-granulation treatment regime on the intensities of OH⁻ band can be followed, and in Figure 11b, the CO₃⁻² band of granulated product can be observed.

Figure 11. FTIR spectra of granulated samples stored in CO₂ atmosphere (15%) in the wavenumber region characteristic to OH⁻ (a) and CO₃⁻² (b).
Therefore, the compressive strength of granules correlated well with the structural changes and chemical reactions taking place during granulation and post-granulation treatment of green granules.

3.3.2. Results of Lysimetric Tests

Granulation of ashes followed by the decrease in leached ions in filtrates. For example, considering the sum of leached ions in filtrates I–III, the content of leached Ca\(^{2+}\) decreased 18\% (from 571 mg L\(^{-1}\) down to 468 mg L\(^{-1}\)) and 26\% (down to 423 mg L\(^{-1}\)), respectively, for stored-dried 24 h at 60 °C and stored before drying 24 h in the atmosphere contained 15\% of CO\(_2\). For ESPA it was 34\% (from 793 mg L\(^{-1}\) down to 525 mg L\(^{-1}\)) for both differently stored granulated samples. For Mg\(^{2+}\) and K\(^{+}\), the decrease was quite miserable for cyclon ash—only 2–6\% (Mg\(^{2+}\) on the level of 40 mg L\(^{-1}\) and K\(^{+}\) of 75 mg L\(^{-1}\)), and not dependent on the post-granulation regime. For ESPA, the decrease of the leached Mg\(^{2+}\) was on the level of 25\% (from 57 mg L\(^{-1}\) down to 43 mg L\(^{-1}\)) and 32\% (down to 39 mg L\(^{-1}\)) in the case of stored-dried 24 h at 60 °C and stored before drying 24 h in the atmosphere contained 15\% of CO\(_2\), respectively. The decrease in the leached K\(^{+}\) was 13\% (from 90 mg L\(^{-1}\) down to 78 mg L\(^{-1}\)) and 20\% (down to 72 mg L\(^{-1}\)), respectively.

The most significant was the decrease of SO\(_4^{2-}\) for cyclon ash 25\% (from 634 mg L\(^{-1}\) down to 466 mg L\(^{-1}\)) and 70\%, (down to 195 mg L\(^{-1}\)) and for ESPA 37\% (from 1090 mg L\(^{-1}\) down to 695 mg L\(^{-1}\)) and 53\% (down to 515 mg L\(^{-1}\)), respectively, dried immediately at 60 °C or after storing in an atmosphere containing 15\% CO\(_2\) [61].

The pH level of soil was improved significantly, from 4.7 up to 6.4 and 5.8 using cyclon ash or ESPA, respectively. No differences were observed in the pH level of soil in the use of initial or granulated OS ashes.

Granulation of OS ashes resulted in the decrease of the content of available Ca\(^{2+}\) in soil on the level of 2–7\% only, and Mg\(^{2+}\) and K\(^{+}\) on the level of 7–12\% only, for both—cyclon ash and ESPA, and it does not depend on the post granulation storing-drying regime. However, the decrease in the content of available SO\(_4^{2-}\) in soil was more significant at storing green granules in the atmosphere containing 15\% of CO\(_2\)—on the level of 18\% and 40\% for ESPA and cyclon ash, respectively [61].

Therefore, granulation of ashes could be a good possibility to prolong the soil neutralizing ability.

3.4. Influence of OS Ash Additives on the Thermal Behaviour of Blends based on Estonian Clays

Thermal and MS Analysis

The results of thermal and MS analysis indicated that at the heating rate of 5 °C min\(^{-1}\), the emission of physically bound water from Arumetsa and Kunda clay continues up to 250 and 270 °C, respectively, with a well-seen respective endothermic minimum in the DTA curve (Figure 12a) and in the water emission profiles (Figure 12b) at 90 °C and 115 °C and with mass loss of 1.77\% and 0.56\%. From the illitic clay, the emission of physically bound water continues up to ~180 °C with a well-seen minimum in the DTG curve and water emission profile at 103 °C (Figure 12) and the mass loss of 0.62\%. At these temperatures takes also place the dehydration of gypsum containing in Kunda clay with a corresponding endothermic minimum in DTA curve at 255 °C.
Figure 12. Thermoanalytical curves (a) and emission profiles of gaseous compounds (b), evolved at thermal treatment of Kunda (K), Arumetsa (A) and illitic (I) clay.

The thermooxidative degradation of organic matter in clays starts at 200–250 °C with characteristic exotherms in DTA curves with a maximum at 312 °C and 315 °C, respectively, for Arumetsa and Kunda clay, and with a shoulder at 310 °C for illitic clay (Figure 12a). The dehydroxylation of clay minerals like illite, illite-smectite, mica, and kaolin takes place between 300–350 °C and 750–800 °C [66–69] with an intensive endothermic minimum in DTA curve at 500 °C and 505 °C, respectively, for Arumetsa and Kunda clay, and at 518 °C for illitic clay (Figure 12a), and with the corresponding peaks minimum in the DTG curve at 497 °C, 501 °C and 480 °C for Arumetsa, Kunda and illitic clay, respectively. The \( \alpha \rightarrow \beta \) quartz transformation in the DTA curve is characterized with the corresponding minimum at 564 °C and 557 °C, respectively, for Arumetsa and Kunda clay, and with the shoulder at 568 °C for illitic clay (Figure 12a) [70].

Emission of water resulted from thermooxidation of organic matter and dehydroxylation of clay minerals occurs between 250 °C and 700 °C in two-three overlapping steps (Figure 12b).

The decomposition of carbonates containing in Arumetsa and Kunda clay takes place between 550–600 °C and 850–900 °C with a characteristic endothermic minimum at 648 °C and 657 °C, respectively, in the DTA curve of Kunda and Arumetsa clay (Figure 12a). In the DTG curve of Arumetsa clay, peaks at 613 °C, 654 °C and 683 °C can be followed, describing, correspondingly, the prolongation of dehydroxylation processes, and decomposition of dolomite and calcite (Figure 12a). In the DTA curve of illitic clay, there is a fixed endothermic shoulder at 630 °C (Figure 12a) characterizing the continuing dehydroxylation processes.

In the emission profiles of \( \text{CO}_2 \) is fixed peaks between 200–250 °C and 500–550 °C corresponding to the thermooxidation of organic matter and, in addition, in the emission profile of Arumetsa clay—another peak with the maximum at 683 °C characterizing the decomposition of carbonates (Figure 12b).

In the DTA curve of Kunda clay, there is a fixed exoeffect with the maximum at 801 °C (Figure 12a) with the corresponding maximum in the \( \text{SO}_2 \)-emission profile at 820 °C.
(Figure 12b) characterizing the second step of thermooxidative decomposition of pyrite [71,72]. The first step of it at temperatures around 400–500 °C is not seen in the DTA curve as it is overlapped with the more intensive endoeffect characterizing dehydroxylation processes occurring at the same temperatures, but it is well fixed in the SO₂ emission profile at around 451 °C (Figure 12b).

The exothermic peak with a maximum in the DTA curves of studied clays at around 930–970 °C (Figure 12a) is characteristic of mullite crystallization [48,73]. The total mass loss heating up to 1050 °C was for Kunda clay 4.8%, for illitic clay 7.3% and for Arumetsa clay 7.9% (Figure 12a).

In thermooxidation of blends containing 60% of clay, 20% of fired clay and 20% of ESPA, some essential differences can be observed comparing with clays without ash additives. For example, replacing a part of beforehand fired clay with ESPA, there were fixed well-seen peaks in the DTG curve at 436 °C and 485 °C (Figure 13a), and maximums in H₂O emission profiles at 436 °C and 496 °C (Figure 13b). These peaks at lower temperatures characterize the decomposition of portlandite and the others dehydroxylation of clay minerals containing, originally, in ESPA and in clays, respectively.

![Figure 13. Thermoanalytical curves (a) and emission profiles of gaseous compounds (b) evolved at thermal treatment of blends containing 60% clay + 20% fired clay + 20% ESPA: Kunda (K), Arumetsa (A), illitic clay (I).](image)

The peak maximums in DTA curves at around 310–320 °C (Figure 13a) and in H₂O and CO₂ emission profiles around 320–330 °C (Figure 13b) corresponding to the thermooxidation of organic matter are less intensive compared with those for clays without ash additives because ashes, except Auvere ash, do not contain organic matter (Table 2). In addition, a part of carbon dioxide formed at thermooxidation of organic matter contained in clays is bound into the solid phase by Ca(OH)₂ or by free CaO giving secondary calcite [74,75]. The maximums in the carbon dioxide emission profiles around 670–680 °C correspond to the decomposition of carbonates contained in clays and in ashes as well as to secondary CaCO₃ formed at lower temperatures (Figure 13b). The total mass loss up to 1050 °C for the blends of Kunda and Arumetsa clay with ESPA additive was 6.3% and 7.4%, respectively, and for the blend of illitic clay 6.6% (Figure 13a).
The thermooxidation of blends containing 60% of clay and 40% of previously hydrated OS ashes is characterized with less intensive mass loss in the temperature intervals between 200–400 °C with a decrease in the intensities of water and carbon dioxide emission profiles comparing with clays or blends with 20% of ash additives according to the decrease of the content of organic matter in blends. Contrary, temperature intervals between 400–500 °C and 550–800 °C are characterized with more intensive mass loss with a corresponding increase in the intensities in H2O and CO2 profiles, respectively, according to the higher content of portlandite and carbonates in blends with 40% of ash additives. From blends based on Kunda clay, the emission of sulphur dioxide into the gaseous phase was not fixed, indicating its total binding into the solid phase by Ca(OH)2 or/and free CaO with the formation of anhydrite [29] which decomposes at temperatures higher than 1050 °C. The total mass loss up to 1050 °C for blends based on Kunda and Arumetsa clay with OS ash was 7.7% and 12.1%, respectively, and for illitic clay, 9.2% [63].

Therefore, the differences in the thermal behaviour of clays and their blends with OS ashes are caused mostly by the differences in their chemical and mineralogical compositions.

4. Conclusions

Thermal analysis, especially combined with evolved gas analysis methods like FTIR and MS, is an excellent tool for studying the thermal behaviour of such complicated objects like oil shale samples, and possible applications for re-use of oil shale ashes in a different area of utilization. The results obtained will serve in the future optimization of technological parameters for the utilization of oil shale ashes.

The results enabled us to determine the multi-step mechanism of thermooxidative decomposition of different oil shale samples, and to identify a number of individual volatile species formed and emitted during the thermooxidation of solid fossil fuels. The differences in the thermal behaviour of different samples are caused by the origin of oil shale: the differences in the chemical matrix of organic matter, chemical and mineralogical composition of inorganic matter, morphology of samples, etc.

The use of thermal analysis technique enabled us to differentiate the potential of different oil shale ashes and the influence of pre-treatment methods (grinding, hydration) on ashes used for the binding of acidic gaseous compounds into the solid phase. It was estimated that moderate grinding with simultaneous moderate water treatment (7 mass%, semidry grinding regime) using Szego Mill™ greatly improved the SO2 binding efficiency of cyclon ash.

The results obtained indicated that the strength and leachability characteristics of granulated oil shale ashes strongly depend on the post-granulation treatment conditions, allowing to increase the neutralizing ability of the granulated products. Thermal analysis/mass-spectroscopy measurements proved that the treatment of green granules in the CO2 containing atmosphere has a crucial role in this.

Thermal analysis combined with evolved gas analysis enabled us to indicate and explain differences in the thermal behaviour of clays and their blends with oil shale ashes depending on the origin of clays and ashes. It was determined that the thermal decomposition of blends followed a two-step decomposition route instead of a one-step, characteristic of clays.

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Abbreviations

| Abbreviation | Description                          |
|--------------|--------------------------------------|
| CFBC         | Circulating fluidized bed combustion|
| DeSOx        | Semi-dry desulphurization system     |
| DTA          | Differential thermal analysis        |
| DTG          | Differential TG                      |
| EGA          | Evolved gas analysis                 |
| EOS          | Estonian oil shale                   |
| ESPA         | Electrostatic precipitator ash       |
| FTIR         | Fourier transform infrared           |
| IOS          | Israel OS                            |
| JOS          | Jordanian OS                         |
| MOS          | Moroccan OS                          |
| MS           | Mass-spectroscopy                    |
| PF           | Pulverized firing                    |
| SSA          | Specific surface area                |
| TG           | Thermogravimetry                     |
| XRD          | X-ray diffraction                    |
| XRF          | X-ray fluorescence                   |

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