Evaluation of New Applications of Oil Shale Ashes in Building Materials

Mustafa Cem Usta 1,*, Can Rüstü Yörük 1, Tiina Hain 2, Peeter Paaver 3, Ruben Snellings 4, Eduard Rozov 5, Andre Gregor 1, Rein Kuusik 1, Andres Trikkel 1 and Mai Uibu 1

1 Department of Materials and Environmental Technology, Tallinn University of Technology, 19086 Tallinn, Estonia; can.yoruk@taltech.ee (C.R.Y.); andre.gregor@taltech.ee (A.G.); rein.kuusik@taltech.ee (R.K.); andres.trikkel@taltech.ee (A.T.); mai.uibu@taltech.ee (M.U.)
2 Department of Civil Engineering and Architecture, Tallinn University of Technology, 19086 Tallinn, Estonia; tiina.hain@taltech.ee
3 Department of Geology, University of Tartu, 50411 Tartu, Estonia; peeter.paaver@gmail.com
4 Sustainable Materials, VITO, 2400 Mol, Belgium; ruben.snellings@vito.be
5 Wienerberger, 43401 Aseri, Lääne-Virumaa, Estonia; eerozedu@gmail.com
* Correspondence: mustafa.usta@taltech.ee

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Abstract: Achieving sustainable zero-waste and carbon neutral solutions that contribute to a circular economy is critically important for the long-term prosperity and continuity of traditional carbon-based energy industries. The Estonian oil shale (OS) sector is an example where such solutions are more than welcome. The combustion of OS generates a continuous flow of ashes destined to landfills. In this study, the technical feasibility of producing monolith building materials incorporating different OS ashes from Estonia was evaluated. Three binder systems were studied: self-cementation of the ashes, ceramic sintering in clay brick production and accelerated carbonation of OS ash (OSA) compacts. Results showed that most of the OSAs studied have low self-cementitious properties and these properties were affected by ash fineness and mineralogical composition. In case of clay bricks, OSA addition resulted in a higher porosity and improved insulation properties. The carbonated OSA compacts showed promising compressive strength. Accelerated carbonation of compacted samples was found to be the most promising way for the future utilization of OSAs as sustainable zero-waste and carbon neutral solution.

Keywords: oil shale ash; waste utilization; concrete; bricks; carbonation curing

1. Introduction

New initiatives by the European Commission not only aim at reducing air and water emissions but also extensively encourage innovation in waste or residue recovery using “Best-Available Technologies” (BAT) that promote transitions towards green energy production under the principles of circular economy [1]. In this context, the Estonian oil shale (OS) sector is a good example where the management and utilization of waste is vital to ensure long term sustainability.

Estonia is still mostly utilizing low calorific fuel—OS as a primary source of energy including electricity, heat and oil production across the country. This heavy fossil fuel reliance produces abundant amounts of uncommon calcareous ash which has been deposited in landfills and waste piles over the years, since the ash lacks industrial applications [2,3]. Historically landfilled ashes as well as the currently generated ashes carry important risks to the biosphere such as emissions of hazardous trace elements (Sr, Zr, As, Cd, Cu, Cr, Zn, Pb) as well as alkalinity to groundwater and air [4–6].

In recent decades the implementation of circulating fluidized bed (CFB) boilers for combustion and advanced retorting technologies for oil production have greatly increased extraction efficiencies
and reduced GHG emissions. However, these changes in the process are not without pitfalls as the physical and chemical characteristics of the OSA were negatively affected. For instance, lowering the temperatures from 1300–1400 °C (previously used in pulverized firing (PF) boilers) to 700–800 °C (used in current CFB boilers) changed the phase composition of the ashes, altered the content of unburnt materials and increased calcium sulfate contents. The phase composition shifted away from high-temperature Ca-silicates towards free lime and quartz. This complicates the utilization of OSA by inducing volumetric expansion and poses environmental issues by increasing the pH of OSAs [7].

The utilization of OSA in the production of new valuable products could be a partial solution for the Estonian OS sector by integrating core concepts from circular economy. In this respect, OSA as any other industrial alkaline solid waste (such as lignite, coal, wood bottom and fly ashes (FAs), steel slags, cement production wastes and waste concrete), can be considered as a valuable raw material in the conventional production processes of cement, concrete and ceramics [8–10]. Evidence of this utilization has existed previously in the Estonian context, where OSA, collected from electrostatic precipitators (EP) of PF units, was used as a raw material for the production of Portland clinker. Additionally, coarse fractions were used as aggregates in the production of cellular concrete blocks and in the applications of road-base stabilization [2,7]. However, due to the above-mentioned changes in the OS incineration process such applications have been phased out. Therefore, there is an urgent need to investigate alternative application routes for OSAs.

The current study includes three sub-studies of oil shale ash utilization in building materials; first sub-study is testing of self-cementing properties of all the currently generated OSAs, second sub-study is the clay brick production with oil shale ash to test its performance as opening agent and the last sub-study is on the properties of OSA monoliths obtained by accelerated carbonation, which draws on the recent developments in research of carbonate bonded construction materials [11–13].

2. Materials and Methods

2.1. Self-Cementing Performance

2.1.1. Materials

A range of OSAs were included in the present study. The selected ashes were mainly FAs regularly collected in the period of 2018 and 2019 including electrostatic precipitator ash (EPA), cyclone ash (CA), total ash (Mixture of all flow of ashes from PP, except EPAs) (TA) and mixtures of different FAs from the Auvere (A) and Eesti (E) power plants (PP). Additionally, CA and TA from the Enefit 280 oil production plant were included. In total, 6 different ash streams (EPP-EPA, EPP-TA, APP-EPA, APP-TA, EN280-CA, EN280-TA) were considered.

2.1.2. Material Characterization

The physical, chemical and mineralogical characterization of the selected waste streams included determination of total carbon (TC) and total inorganic carbon (TIC) with an Eltra CS 580 (Haan, North Rhine-Westphalia, Germany) Carbon Sulphur Determinator and free CaO content (based on ethylene glycol method), X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses with Bruker S4 Pioneer (Karlsruhe, Baden-Württemberg, Germany) and Bruker D8 (Karlsruhe, Baden-Württemberg, Germany) diffractometers, respectively. For XRD analysis, randomly oriented preparations were made and scanned on a Bruker D8 Advance diffractometer using Cu Kα radiation with a Göbel mirror monochromator and LynxEye positive sensitive detector over a 2°–70° 2Θ range. The quantitative phase composition was analysed and modelled using the Rietveld algorithm-based program Topas (Karlsruhe, Baden-Württemberg, Germany). The relative error of quantification is better than 10% for major phases (>5 wt. %) and better than 20% for minor phases (<5 wt. %). The BET-N₂ sorption method was used to measure the specific surface area (SSA) with Kelvin 1042 sorptiometer.
The particle size distribution (PSD) was measured by laser diffraction using a Horiba (Kyoto, Japan) Laser Scattering instrument, LA-950 (with ethanol suspension).

### 2.1.3. Sample Preparation

In order to test the self-cementing properties of the OSAs, ash and sand pastes were prepared for all waste streams. 0.7 was found to be optimum ratio of water to ash [14] and ash to sand (cf. EN 196-1:2016) ratio was 0.33. Pastes were cast in $40 \times 40 \times 160 \text{ mm}^3$ prisms and compacted using a vibration table. The compacted pastes were first kept 48 h in molds, then five days at 60% RH and $20 \pm 2 ^\circ \text{C}$, and further curing continued for 28 days at $>95% \text{ RH}$ and $20 \pm 2 ^\circ \text{C}$. After 28 days, the failure strength (flexural and compressive strength) was tested following EN 196-1:2016 [15].

The aim of the work regarding self-cementing properties of oil shale ashes was to find possibilities for utilization of oil shale ashes. These types of studies are based on our own experience with oil shale throughout the years. The methods described therein might vary from those utilized in the applications of Portland cements due to the distinct influence of OSA types and properties of pastes and mortars.

### 2.1.4. Tests and Measurements

Flexural strength test determined the maximum bending stress of prisms before failure. This test was conducted on a Toni TechnikD-13355 (Berlin, Brandenburg, Germany) which works in accordance with EN ISO 7500-1 (2018) [16]. The compressive strength test was also performed using the same apparatus which applies a progressing load rate of 2400 N/S in accordance with EN 196-1:2016 and ISO 679 [17]. The split mortar bar halves from flexural strength test were used for the compressive strength measurements.

### 2.2. Clay Bricks with Sand to OSA Replacement

#### 2.2.1. Materials

The clay (Cambrian blue clay) and clay/sand mixtures used in the green shaped bodies were obtained from Wienerberger Company—located in Aseri, Estonia. Similar physical and chemical characterization methods, as defined above for concrete application, have been used for the material characterization of the clay.

The studied OSA sample for clay bricks is EPP-EPA obtained in August 2018 which was separated into different size fractions by size classification. The coarse fraction was used as sand or opening agent replacement in the formulation of clay bricks. Material characterization considered both the initial EPP-EPA and coarse fraction of EPP-EPA in terms of PSD, SSA, XRF and XRD analyses.

#### 2.2.2. Sample Preparation

In a first trial stage 3 brick formulations were tested. A reference brick was prepared with a mixture ratio of 80% clay/20% sand. A constant brick formulation of 80% clay/10% sand/10% EPP-EPA was used for both the initial and coarse ash. Bricks were prepared in triplicate by hand.

The obtained fresh clay was first dried in a ventilated oven at 105 °C for 4 h. Dried agglomerates were comminuted using a ball mill for 20 min. Subsequently, the clay was ground to fine powder using a four-ball planetary mill (clockwise rotation for 10 min at 350 rpm, anti-clockwise rotation for 5 min at 350 rpm) and dried again at 105 °C for 4 h. The dried raw materials were mixed in the specified ratios and water was added to obtain similar plasticity (sight/feeling) of the mixtures. An infrared moisture analyzer was used to measure the water content of the mixtures. For EPP-EPA added bricks 20 wt. % water was used while 15 wt. % water was required for the reference bricks. The pastes were placed into $40 \times 40 \times 160 \text{ mm}^3$ prisms and a hydraulic press applied a pressure of 75 kg/cm² for 10 s. After demolding, the prepared green bodies were left to dry; first at room temperature (12 h) then in a drying chamber (with slow temperature ramp (~15 °C/h) up to 105 °C) until water evaporation related mass change stops before transferring them to the sintering stage. This process was carried
out to avoid possible swelling or cracking of the samples in the furnace, caused by the expansion of entrapped water. Finally, the samples were sintered at 1020 °C which took approximately 48 h (including slow heating and cooling cycle) in an industrial tunnel furnace under oxidizing conditions.

2.2.3. Tests and Measurements

After press molding, the samples were weighed, and dimensions were measured to calculate the wet density. The same process was repeated after drying and sintering to obtain both dry density and end product density values. A water absorption test was carried out according to EN 771-1:2011 + A1:2015 [18]. The flexural and compressive strength tests were performed with Toni TechnikD-13355 (Berlin, Brandenburg, Germany). The thermal conductivity test was carried out with a HOT DISK TPS 2200 (Gothenburg, Västra Götaland County, Sweden) instrument which meets the ISO 22007-2 standard [19]. The intact samples were used for this analysis. The hot disk Teflon sensor was placed on opposite intact sides of the bricks and the thermal conductivity was measured at a rate of 10 K/s. The experiment is repeated on different sides of the same bricks and the mean value was recorded for further calculation. Porosity measurements were carried out with a POREMASTER PV007130 (Graz, Styria, Austria) which uses three automatic mercury intrusion cycles for pore size analysis. Measurements focused on intraparticle porosity which is the porosity within individual grains or particles. Total porosity was also measured to gain insight in all void spaces regardless of interconnectivity. In order to investigate the microstructure of the sintered bricks SEM images were obtained from the polished samples using a ZEISS Evo MA 15 (Oberkochen, Baden-Württemberg, Germany). The mineralogical composition was determined using XRD analysis.

2.3. Accelerated Carbonation of Compacted Samples

APP-EPA (October 2018) was chosen as starting material for the preliminary tests of compacted cylinders (Figure 1) as APP-EPA is enriched in free lime, therefore more suitable for carbonation purposes. A representative sample was taken and divided into two size fractions (fine (0–100 µm) and coarse (100–300 µm)) by sieving in order to investigate the effect of particle size on compaction behavior of ashes and extent of carbonation.

![Figure 1. 100% APP-EPA compacted cylinders.](image-url)

2.3.1. Sample Preparation

The accelerated carbonation process consisted of three main steps; the first step was proportioning of selected APP-EPA and prehydrating the sample to slake the free lime, the second step was the compaction of the sample using a hydraulic press and the third step was the carbonation of the product in an autoclave. In the first step the samples were mixed with water at a liquid to solid mass ratio of 0.25 in a semi-batch Eirich EL1 (Hardheim, Baden-Württemberg, Germany) type intensive mixer. The samples were homogeneously blended with water at a rotation speed of 600 rpm for 30 min. The samples were left to hydrate/cure in closed plastic bags overnight at room temperature and compacted on the following day using a hydraulic press into cylinders with diameter 20 mm and height 20 mm at a compaction pressure of 300 kg/cm². Carbonation experiments were performed in automated...
carbonation units consisting of a temperature controlled stainless-steel autoclave. The autoclave was operated at two different pressure levels while temperature stayed at ambient levels; the compacted specimens were placed in the autoclave and cured by applying 100% CO$_2$ gas pressure of 5 and 10 bar for 4 h.

2.3.2. Tests and Measurements

The obtained results from compressive strength measurements were used as main parameter to evaluate the performance of the carbonated monoliths. The CO$_2$ uptake during carbonation was determined by thermogravimetric analysis (TGA). Additionally, XRD measurements were made to follow the formation of new phases during the carbonation process.

3. Results and Discussions

3.1. Oil Shale Ash Material Characterization

The BET specific surface area (SSA) and the mean particle size of the OSAs considered in this paper are summarized for APP (EPA, TA) in Figure 2, and for EPP (EPA, TA) and EN280 (TA, CA) in Figure 3. The variation of the physical properties is shown for different sampling dates. In case of APP OSA, EPA shows consistently finer particle sizes than TA, even though BET SSA fall within the same range. The EPP EPA and TA do not show this difference in particle size and are somewhat coarser (Appendix A: Tables A1 and A2). The particle size of EN280-TA is coarser than EN280-CA and showed a correspondingly lower SSA.

![Figure 2. Particle size and BET SSA for APP (EPA, TA).](image)

![Figure 3. Particle size and BET SSA for EPP (EPA, TA) and EN280 (TA, CA).](image)
All OSAs studied mainly consist of SiO$_2$, CaO and Al$_2$O$_3$, however in variable proportions (Figure 4). The main reason of such differences could be explained with several factors including characteristics of raw OS, OS processing conditions, thermochemical conversions, gaseous treatments for cleaning, boiler specifications, etc.

In general, the high content of CaO can be explained by the decomposition of CaCO$_3$ which originally exists in the mineral part of OS and partially decomposes during the thermal processes. The presence of SiO$_2$ can be attributed to the inorganic part of the OS and mainly is representing finer particles as the content of silica is higher and lime content is lower in smallest size fractionated ashes. The chemical composition of OSAs differs and each type appears to show a distinct composition (Appendix B: Table A3). For instance, the high LOI of the EN280 residues is related to the lower temperature processing during retorting compared to combustion of OS causing delay in decomposition of carbonates and oxidation of unburnt carbon. Specifically, in case of EN280 TA, the high LOI of the residue correlates with a low SSA and coarse PSD which are all negative factors in terms of self-cementing behavior of these types of ashes especially when it is considered that fly ashes with high LOI can negatively affect the strength of the concrete (more water absorption, air-entraining, etc.) and increase setting times [20,21].

The variations in chemical composition are reflected in the phase composition as well as shown in Tables 1–3. Some fluctuations in phase composition of the ashes were observed throughout the year in the EPA fractions. The amount of free CaO is higher than 10% for EPP and APP ashes (EPA, TA) and mineral CO$_2$ content does not reach above 11%. Calcite and dolomite contents of EN280-CA and TAs are quite high, and the content of Ca/Mg silicates (C$_2$S, akermanite, mervinite) and aluminates are quite low compared to all other studied samples due to the low temperature processing during retorting.
The samples that were used in last two sub-studies do not include ashes from oil shale retorting and these sub-studies only focus on the ashes produced from the combustion of oil shale. Both ashes used in the sub-studies are fly ashes (70% of the total ash produced) collected from electrostatic precipitators where most of the ash is accumulated during the combustion of oil shale. By studying these ashes throughout the year, we noticed that the minerology, chemical and physical properties do not change drastically. Another important factor for selecting the ashes in the last two sub-studies, is the content of free CaO.
Table 3. Phase composition of EPP (EPA, TA).

| Phase      | EPP EPA 15.5.2018 | EPP EPA 06.02.2018 | EPP TA 06.02.2018 |
|------------|-------------------|-------------------|-------------------|
| Quartz     | 18.1              | 19.9              | 17.0              |
| K-feldspar | 13.9              | 15.5              | 12.7              |
| Mica       | 5.4               | 4.7               | 4.5               |
| Calcite    | 15.1              | 8.1               | 11.1              |
| Dolomite   | tr                | -                 | -                 |
| Hematite   | 2.1               | 2.4               | 2.0               |
| Lime       | 7.0               | 12.7              | 14.0              |
| Portlandite| 2.2               | -                 | 1.5               |
| Periclase  | 4.8               | 4.1               | 5.0               |
| Anhydrite  | 9.7               | 11.4              | 11.0              |
| C$_2$S     | 9.2               | 4.9               | 5.6               |
| C$_4$AF    | 4.1               | 2.4               | 2.7               |
| Akermanite | 4.5               | 8.6               | 8.2               |
| Merwinites | 1.6               | 3.6               | 3.8               |
| Sylvite    | 1.2               | -                 | -                 |
| Wollastonite| -                 | 1.3               | 1.1               |

3.2. Self-Cementing Properties of Oil Shale Ash

Self-cementing ability and setting times of the considered OSAs are shown in Figures 5 and 6. The self-cementing ability is affected by the chemical composition and fineness of ashes, in particular the content of free CaO, portlandite, Ca/Mg silicates and SO$_3$ [22,23]. The self-cementing ability of ashes with coarse particle sizes and lowest temperature of treatment is generally lowest. This is demonstrated for EN280-CA and TAs.

![Figure 5](image-url)
Figure 5. Setting times and self-cementitious ability for APP-EPA and APP-TA.

Figure 6. Setting times and self-cementitious ability for EPP (EPA, TA) and EN280 (TA, CA).

Comparing the self-cementing properties of all studied ashes, the performance of the APP-EPA and APP-TA was found to have better properties. Between these two samples of ashes, APP-EPA is shown to have optimal suitability. This is tentatively explained by a higher BET SSA and a considerable content of lime and portlandite (~14–23%), Ca-Mg silicates (C₃S) and C₄AF (~15–22%) that can participate in hydraulic or pozzolanic reactions. Therefore, APP-EPAs and EPP-EPAs have potential self-cementing properties.

Setting times were tested according to EN 196-3:2016 in order to evaluate how long the samples remain in a plastic state that enable placing or casting the mixes. However, most of the studied mixes demonstrated very short setting times. This is tentatively related to the quick hydration of free CaO [24].

Because of this reason, less reactive ashes (EN280) would require post-treatments like higher temperature treatment, grinding, sieving etc. in order to increase their performance. Due to insufficient amounts of reactive phases present the EN280 ash specimens fell apart during the curing of samples as cohesion is lost after evaporation of water in the 60% RH environment (Figure 7).

Figure 7. Spontaneous disintegration of EN280 specimens after 60% RH curing.
3.3. Clay Brick Production Using OSA

It can be seen from Table 4 that EPP-EPA has more complex and different chemical composition than the clay which mostly consists of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ and K$_2$O. The main oxides in EPP-EPA are SiO$_2$—31.94%, CaO—35.25%, Al$_2$O$_3$, MgO and the content of SO$_3$ is relatively high as well. The LOI is 4.8% due to the release of combined water, crystalline water, combustion of organic carbon and oxidation of sulfur.

Table 4. Chemical composition of EPP-EPA and clay.

| Oxides        | EPP EPA (wt. %) | Clay (wt. %) |
|---------------|----------------|--------------|
| CaO total     | 35.25          | 0.4          |
| MgO           | 5.85           | 2.3          |
| SiO$_2$       | 31.94          | 61.4         |
| Al$_2$O$_3$   | 7.46           | 17.8         |
| Fe$_2$O$_3$   | -              | 5.9          |
| SO$_3$        | 7.12           | 1.6          |
| K$_2$O        | 3.32           | 6.1          |
| Na$_2$O       | 2.28           | 0.08         |
| Mn$_2$O$_3$   | 0.06           | -            |
| TiO$_2$       | 0.38           | -            |
| P$_2$O$_5$    | 0.14           | -            |
| LOI *         | 4.82           | 4.8          |
| TOC *         | 0.22           | 0.21         |

* LOI—Loss on ignition; TOC—Total organic carbon.

The mineralogy of the clay shows a heterogeneous mixture of minerals (Table 5) and can be subdivided into clay minerals (~60%) including kaolin, illite, illite-smectite, mica and chlorite, and non-clay minerals (~40%) including mainly quartz, orthoclase and minor constituents such as gypsum, pyrite and calcite. The clay used in this work is also characterized by a higher BET SSA—30.86 m$^2$/g and smaller mean particle size (15.1 $\mu$m).

Table 5. Phase composition of EPP-EPA and clay.

| Phases                  | EPP EPA (wt. %) | Clay (wt. %) |
|-------------------------|----------------|--------------|
| Quartz                  | 16.1           | 27.2         |
| Free Lime               | 12.6           | -            |
| Anhydrite               | 9.1            | -            |
| Calcite                 | 8              | 0.3          |
| Kaolin                  | -              | 7.1          |
| Periclasmande            | 3.8            | -            |
| Hematite                | 2.9            | -            |
| beta C$_2$S             | 2              | -            |
| gamma C$_2$S            | 4.4            | -            |
| C$_4$AF                 | 2.1            | -            |
| Mullite                 | 0              | -            |
| Pyrite                  | -              | 0.8          |
| Ca-langbeinite          | 2.5            | -            |
| Gypsum                  | -              | 1.2          |
| Chlorite                | -              | 5.1          |
| Orthoclase              | 4.5            | 5.2          |
| Illite, Illite-smectite, Mica | 3.6         | 52.2         |
| Amorphous               | 28.3           | -            |

Based on the observations made on prepared samples, as a first impression it can be mentioned that the color is one of the parameters to consider when producing bricks, as different type of ashes
would lead to significant changes in color when compared with the reference bricks. It can be observed in Figure 8, EPP-EPA does make the color of bricks lighter and give a new yellowish color.

![Figure 8](image_url)

**Figure 8.** (a) Reference 4:1 clay:sand, (b) 8:1:1 clay:sand:EPP-EPA coarse and (c) 8:1:1 clay:sand:EPP-EPA.

The densities of bricks after molding, drying and sintering are presented in Table 6. Dry densities are lower than wet densities and values are proportional to the required initial water content for molding the bricks. The reaction between free CaO and water bonds water chemically which makes the dry density not exactly proportional to initial water added to the EPP-EPA added raw mixtures. It can also be seen that the values of reference bricks show a noteworthy increase in density after sintering while the density of EPP-EPA added bricks show only a slight increase. The shrinkage of bricks after sintering is given based on the volume changes and it can be noted that the reference bricks have the highest shrinkage. With the addition of EPP-EPA, a notable reduction of shrinkage can be explained due to the different phase composition of EPP-EPA compared to sand which is mainly inert and as a result accompanies different volume reduction. The presence of Ca(OH)$_2$, Ca and Mg carbonates, partially Ca- sulphate (the decomposition of sulphates can proceed well below 1000 °C in presence of CO [25]) in EPP-EPA strongly influences the brick microstructure by releasing H$_2$O, CO$_2$ and SO$_2$ due to the new decomposition reactions attributed to EPP-EPA (Equations (1)–(4)) in addition to clay mineral dehydroxylation, quartz inversion, crystallization and formation of vitreous phase reactions [26].

\[
\begin{align*}
\text{Ca(OH)}_2 & \rightarrow \text{CaO} + \text{H}_2\text{O} \quad (1) \\
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \quad (2) \\
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2 \quad (3) \\
\text{CaSO}_4 + \text{CO} & \rightarrow \text{CaO} + \text{SO}_2 + \text{CO}_2 \quad (4)
\end{align*}
\]

| Physical Properties | Reference | EPP-EPA Initial | EPP-EPA Coarse |
|---------------------|-----------|----------------|----------------|
| Wet Density (kg/m$^3$) | 2138 | 1868 | 1818 |
| Dry Density (kg/m$^3$) | 1845 | 1779 | 1744 |
| Sintered density (kg/m$^3$) | 2185 | 1723 | 1766 |
| Sintering shrinkage (%) | 12 | 5 | 6 |

The physical and performance properties of the bricks are affected by the increased porosity of the EPP-EPA bricks. The compressive and flexural strength constitute the main parameters of brick performance. The obtained average value for the compressive strength EPP-EPA added bricks was ~20 MPa and for reference bricks ~30 MPa. These results correlate with the increased porosity of the EPP-EPA bricks as higher water absorption is usually associated with higher porosity as well. Water absorption values (Table 7) showed lowest water absorption for the reference bricks and EPP-EPA addition led to an increase in water absorption value (2.5 times).
Table 7. Mechanical and thermal properties of bricks.

| Sample Name         | Compressive Strength (MPa) | Flexural Strength (MPa) | Water Absorption (%) | Thermal Conductivity (W/mK) |
|---------------------|-----------------------------|-------------------------|----------------------|----------------------------|
| Reference           | 30.6                        | 8.9                     | 5.2                  | 1.22                       |
| EPP-EPA initial     | 21.5                        | 4.2                     | 13.9                 | 0.67                       |
| EPP-EPA coarse      | 19.3                        | 4.4                     | 13.3                 | 0.71                       |

Thermal properties are important in terms of heat insulation and energy performance of buildings. The thermal conductivity of a composite material is determined by the properties of its constituents. In case of clay bricks the thermal conductivity varies depending on porosity and conductivity of the solid constituents and exhibits a decrease in trend with bulk density [27]. It can be seen from the measured thermal conductivity values of the fired bricks, given in Table 7, that EPP-EPA bricks have 50% better insulation properties than the reference bricks.

An overall porosity reduction is expected when above 1000 °C the vitreous phase fills the pores and the ceramic body shrinks. From the porosity results shown in Figure 9, it can be understood that the EPP-EPA samples show a higher volume of pore features in the range of 0–4 µm compared to the reference.

Additionally, the SEM images of the brick samples are shown in Figure 10 and it is evident that a higher degree of particle interlocking, and more homogeneous texture can be observed for the reference brick microstructure.

The presence of carbonates strongly influences the brick microstructures and lowers the degree of shrinkage. This is partially due to the additional porosity generated during decomposition of the Ca carbonate into free lime and CO\textsubscript{2} gas (Equation (2)). The CaO further recombines with the clay minerals during crystallization reactions and results in changes of the brick phase composition. Similar findings were also mentioned in other studies (Junge [28], Sütcü and Akkurt [29]) where other waste additives with high CaCO\textsubscript{3} content (i.e., paper making sludge, limestone powder) were evaluated for brick production and these types of residues were identified as pore-forming additives.

The phase composition of the EPP-EPA and the reference bricks is compared in Table 8, the main difference is the presence of a significant fraction of plagioclase (Ca-feldspar) in the EPP-EPA bricks. In addition, small amounts of anhydrite and mullite were identified as well. Clearly CaO introduced by the EPP-EPA reacted with the aluminosilicates in the clay to form plagioclase feldspar. Anhydrite did not decompose fully during the sintering.

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \quad (2) \]

\[ \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \quad (3) \]

\[ \text{CaSO}_4 + \text{CO} \rightarrow \text{CaO} + \text{SO}_2 + \text{CO}_2 \quad (4) \]
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Figure 10. The SEM images of the brick samples, (a) Reference sample, (b) EPP-EPA (coarse).

Table 8. Phase composition of Reference and EPP-EPA added bricks (coarse).

| Phase       | Reference (wt. %) | EPP-EPA (wt. %) |
|-------------|------------------|-----------------|
| Quartz      | 58.0             | 31.3            |
| K-feldspar  | 12.6             | 20.8            |
| Plagioclase | -                | 17.7            |
| Mica        | 3.6              | 6.03            |
| Hematite    | 3.8              | 4.5             |
| Anhydrite   | -                | 2.1             |
| C2S         | -                | 1.3             |
| C4AF        | -                | 0.5             |
| Sanidine    | 9.7              | -               |
| Spinel      | 11.8             | 10.2            |
| Mullite     | -                | 3.7             |

3.4. Carbonate Bound Monolith Production from Oil Shale Ash

CaO/MgO and Ca/Mg-silicates in OSA are potential phases for CO2 sequestration via carbonation. By carbonation of compacted samples, CO2 can be permanently stored as Ca or Mg carbonates. The formation of carbonates is associated with an increase in solid volume and a decrease in porosity of the compacts. The carbonates act as cement by forming solid bridges between reacting particles and infilling of porosity.

The compressive strength test results of the compacted APP-EPAs are quite promising and compacts that are made of coarser fraction have greater compressive strength (up to 41.4 MPa) for both tested pressure levels (Table 9). Interestingly, the compacts carbonated at 5 bar show higher strength values compared to 10 bar. This may suggest that high pressures lead to fast reactions causing pore clogging near the surface of the compacts and zonation instead of homogeneous carbonation. In fact, previous studies have also shown that excess CO2 pressure does not necessarily lead to a higher compressive strength as slower reaction would allow for dissipation of heat and reduce stresses on the product [30]. Further research into the microstructure of the carbonated compacts is needed to verify the mechanism controlling the carbonation reaction and to further optimize the performance of the carbonated products.
Table 9. Compressive strength, water absorption and density results for carbonated APP EPA compacts.

| Particle Size (µm) and Pressure (bar) | Compressive Strength (MPa) | Density (kg/m³) | Water Absorption (%) |
|--------------------------------------|----------------------------|-----------------|---------------------|
| 0–100 µm 5 bar                       | 24.9 ± 4.5                 | 1992            | 11.2                |
| 0–100 µm 10 bar                      | 8.6 ± 1.3                  | 1807            | 12.3                |
| 100–300 µm 5 bar                     | 38.1 ± 1.9                 | 1882            | 9.8                 |
| 100–300 µm 10 bar                    | 20.1 ± 1.6                 | 1675            | 10.4                |

Thermogravimetric analysis measurements of the compacts made from coarse fraction of APP EPA are presented in Figure 11. The mass loss due to the release of CO₂ that is related to decomposition of carbonates is indicated for the uncarbonated sample as well as it already includes CaCO₃ in the raw untreated ash which is measured as 6%. The samples cured at 5 and 10 bar show higher mass loss which is related to the mineral CO₂ bounded during carbonation, indicating that the CO₂ uptake during the carbonation treatment can be up to ~9% of the total mass of the sample.

![Figure 11. TGA curves for monoliths made from coarse fraction of APP EPA.](image_url)

The phase composition of the uncarbonated and carbonated compacts are given in Table 10. Portlandite Ca(OH)₂ and ettringite are major phases present in the uncarbonated sample. In the carbonated samples a strong increase in the calcite (CaCO₃) fraction is notable. Calcite appears to form mainly at the expense of portlandite and ettringite. Additional to calcite, some gypsum has formed by carbonation of ettringite. Also, C₂S and merwinite appear to have partially carbonated. As noticed as well in the TGA, portlandite is not fully consumed indicating that further improvement of the process is possible. The fine ash fraction of 0–100 µm shows differences in its initial phase composition being higher in quartz, K-feldspar and mica and lower in anhydrite phases. This is reflected in the phase composition of the carbonated material.
Table 10. Phase composition of monoliths.

| Phase     | 100–300 µm Uncarbonated | 0–100 µm 5 bar | 100–300 µm 5 bar | 100–300 µm 10 bar |
|-----------|-------------------------|----------------|------------------|------------------|
| Quartz    | 5.4                     | 12.7           | 4.6              | 5                |
| K-feldspar| 1.5                     | 14.4           | 1.7              | 1.4              |
| Mica      | -                       | 3.1            | -                | -                |
| Calcite   | 10.2                    | 43.5           | 35.1             | 38.4             |
| Dolomite  | 1.9                     | 3.1            | 2.7              | 3.6              |
| Anhydrite | 16.1                    | 5.9            | 16.9             | 16.2             |
| Periclase | 2.4                     | 2.6            | 3.6              | 3.9              |
| Portlandite| 36.1                    | trace          | 17.2             | 15.4             |
| Vaterite  | -                       | 0.5            | -                | -                |
| Akermanite| 1.8                     | 4              | 2.2              | 1.6              |
| Merwinite | 3                       | 0.5            | 1.5              | 1.5              |
| C₂S       | 4.7                     | 0.8            | 1.6              | 1.3              |
| Hematite  | 1.1                     | 2.2            | 1                | 0.8              |
| Ettringite| 10.1                    | 1.9            | 5.7              | 4.5              |
| Gypsum    | 0.7                     | 4.1            | 2.9              | 3.9              |
| Brucite   | 4.7                     | trace          | 3                | 2.5              |

4. Conclusions and Perspectives

Estonian oil shale ash (OSA) characterization results showed that the new types of OSA from Enefit280 units contain significantly less free lime and more undecomposed carbonates compared to other combustion technologies. Additionally, chemical and physical composition of this type of ash is quite variable throughout the testing period of this study. In contrast, both the chemical and physical composition of APP and EPP ashes stay practically unchanged providing easier implementation of storage or recycling treatments.

APP-EPA is the only type of ash which can be considered as an independent potential binder. The rest of the tested ashes would require additional physical or thermal pre-treatments to make them fit for use in cement and concrete applications. These types of wastes for instance could be re-evaluated as a composite raw material for mixed binders including other constituents.

The effect of EPP-EPA addition was investigated in terms of physical, mechanical and thermal properties of clay bricks. From a broad perspective it can be concluded that the physical, mechanical and thermal properties (i.e., workability of raw mixtures, water absorption, color, texture, density, porosity, strength, and thermal conductivity) of the produced bricks are affected by the composition of the OSA. There is a continuous effect of the exothermic CaO–H₂O reaction (forming Ca(OH)₂) being active as soon as raw materials are in contact with water and prolonged even after press molding which may cause slight expansion and higher porosity already before the firing stage. Further, release of bound water due to the decomposition of hydrates and decomposition of Ca(OH)₂, CaCO₃ and partially CaSO₄ lead to the creation of additional porosity during the firing process. In this respect, EPP-EPA and similar OSAs or carbonate rich wastes with high reactive free lime content can be considered as pore forming agent for clay bricks and applications require specific care to control the product performances.

From a technical point of view, the results obtained from accelerated carbonation of compacted APP-EPAs demonstrate that this type of compaction and carbonation process can be a promising way of waste utilization as it provides a way to produce valuable construction materials with high material strength while also binding CO₂. In this context, efforts and studies should proceed to further develop and optimize this process for OSA in order to improve the extent of the carbonation and produce specific building materials, for instance with good thermal and sound insulation characteristics.

To conclude, the results presented in this study indicate potentially interesting pathways for OSA utilization and all observations provide a basis of the future optimization of OSA combustion and treatment processes in view of utilization of the generated ashes.
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Abbreviations

OSA Oil Shale Ash
CFB Circulating fluidized bed
PF Pulverized firing
EPA Electrostatic precipitator ash
CA Cyclone ash
TA Total ash
FA Fly ash
EPP Estonian power plant
APP Auvere power plant
EN280 Enefit 280 shale oil plant
PSD Particle size distribution
SSA Specific surface area
XRF X-ray fluorescence
XRD X-ray diffraction
TGA Thermogravimetric analysis

Appendix A

Table A1. Particle size distribution of EPP and EN280 ashes (d50, d90, d10).

| Name | Type | Date       | d50 | d90  | d10 |
|------|------|------------|-----|------|-----|
| EPP  | EPA  | 02.06.2018 | 37.3| 74.2 | 10.1|
| EPP  | EPA  | 05.15.2018 | 42.8| 74.2 | 10.1|
| EPP  | TA   | 02.06.2018 | 44.0| 89.5 | 10.6|
| EPP  | TA   | 02.09.2018 | 280.8| 934.5| 8.1 |
| EN280| TA   | 07.12.2018 | 36.9| 279.4| 8.1 |
| EN280| TA   | 10.30.2018 | 28.6| 279.4| 8.1 |
| EN280| TA   | 03.19.2019 | 31.2| 279.4| 8.1 |
| EN280| CA   | 07.12.2018 | 22.5| 74.2 | 10.1|
| EN280| CA   | 10.30.2018 | 21.3| 74.2 | 10.1|
| EN280| CA   | 03.19.2019 | 34.7| 74.2 | 10.1|

Table A2. Particle size distribution of APP ashes (d50, d90, d10).

| Name | Type | Date       | d50 | d90  | d10 |
|------|------|------------|-----|------|-----|
| APP  | EPA  | 02.15.2018 | 21.9| 57.1 | 7.7 |
| APP  | EPA  | 05.12.2018 | 23.1| 42.3 | 7.1 |
| APP  | EPA  | 08.09.2018 | 23.0| 44.2 | 8.9 |
| APP  | EPA  | 10.25.2018 | 22.0| 45.3 | 8.4 |
| APP  | EPA  | 03.13.2019 | 23.2| 75.3 | 7.7 |
| APP  | TA   | 02.21.2018 | 31.4| 73.1 | 7.7 |
| APP  | TA   | 05.12.2018 | 32.9| 51.2 | 7.1 |
| APP  | TA   | 07.10.2018 | 28.7| 64.7 | 8.9 |
| APP  | TA   | 10.25.2018 | 34.2| 65.2 | 7.7 |
| APP  | TA   | 03.13.2019 | 37.6| 75.7 | 8.4 |
Appendix B

Table A3. Chemical composition of all oil shale ashes.

| Component | SiO₂ | Al₂O₃ | TiO₂ | Fe₂O₃ | MnO | CaO | MgO | Na₂O | K₂O | P₂O₅ | SO₃ | LOI |
|-----------|------|-------|------|-------|-----|-----|-----|-------|-----|------|-----|-----|
| Unit      | mass%| mass% | mass%| mass% | mass%| mass%| mass%| mass% | mass%| mass% | mass%| mass%|
| APP TA 25.10.2018 | 20.5 | 4.8  | 0.2 | 2.9  | 0.1 | 42.4 | 3.8 | 0.1  | 2.5 | 0.2  | 5.2 | 15.0 |
| APP EPA 25.10.2018 | 27.1 | 6.3  | 0.3 | 3.1  | 0.0 | 39.3 | 2.9 | 0.4  | 3.1 | 0.1  | 3.8 | 12.5 |
| APP EPA 13.03.2018  | 22.0 | 5.2  | 0.2 | 3.6  | 0.1 | 39.1 | 7.2 | 0.3  | 2.2 | 0.1  | 6.7 | 11.2 |
| APP TA 13.03.2018   | 22.3 | 5.2  | 0.2 | 3.2  | 0.1 | 40.3 | 5.5 | 0.1  | 2.5 | 0.1  | 6.5 | 12.2 |
| APP EPA 09.08.2018  | 22.6 | 6.3  | 0.3 | 3.2  | 0.0 | 38.9 | 2.8 | 0.2  | 3.0 | 0.1  | 4.3 | 12.6 |
| APPTA 12.05.2018    | 17.3 | 4.0  | 0.2 | 2.7  | 0.1 | 43.1 | 5.1 | 0.1  | 2.1 | 0.2  | 5.0 | 17.8 |
| EPP EPA 06.02.2018  | 35.8 | 11.3 | 0.7 | 5.5  | 0.1 | 27.3 | 4.4 | 0.1  | 4.5 | 0.1  | 5.6 | 4.0  |
| EPP EPA 06.02.2018  | 30.8 | 9.6  | 0.6 | 5.2  | 0.1 | 32.2 | 4.9 | 0.1  | 3.7 | 0.1  | 5.6 | 6.5  |
| EPP EPA 15.05.2018  | 33.2 | 7.8  | 0.4 | 4.0  | 0.1 | 30.0 | 4.9 | 0.2  | 3.5 | 0.1  | 4.8 | 8.3  |
| EN280 TA 19.03.2019 | 6.7  | 1.4  | 0.1 | 1.8  | 0.0 | 48.1 | 3.2 | 0.1  | 0.6 | 0.1  | 4.1 | 34.5 |
| EN280 CA 19.03.2019 | 29.9 | 7.0  | 0.3 | 3.7  | 0.0 | 29.0 | 3.4 | 0.1  | 3.5 | 0.1  | 4.5 | 17.3 |
| EN280 TA 30.10.2018 | 5.2  | 1.2  | 0.1 | 1.4  | 0.1 | 49.0 | 3.3 | 0.1  | 0.4 | 0.1  | 2.3 | 37.7 |
| EN280 CA 30.10.2018 | 28.3 | 6.7  | 0.3 | 3.6  | 0.1 | 29.2 | 3.6 | 0.2  | 3.3 | 0.1  | 4.7 | 18.0 |
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