TALLINNA TEHNIKAÜLIKOOL
TALLINN UNIVERSITY OF TECHNOLOGY

Department of Materials and Environmental Technology

UTILIZATION OF FLY ASH IN CLAY BRICKS

LENDTUHA KASUTAMINE SAVITELLISTES

MASTER THESIS

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Tallinn, 2019

AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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Department of Materials and Environmental Technology

THESIS TASK

Student : Deepak Sundar Mohan, 177343KAYM

Study program : KAYM, Materials and Processes of Sustainable Energetics

Main specialty : Processes of Sustainable energetics

Supervisor : Engineer, Can Rüstü Yörük

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Thesis topic:

(in English) UTILIZATION OF FLY ASH IN CLAY BRICKS

(in Estonian) LENDTUHA KASUTAMINE SAVITELLISTES

Thesis main objectives:

1. Utilizing oil shale and coal fly ash in fired clay brick produciton.
2. Prepare Flyash bricks and perform experiments to define the level of reliability.

Thesis tasks and time schedule:

No	Task description	Deadline
1.	Review of available literature related to Fly ash utilization in bricks	10.01.2019
2.	Prepare required materials and perform experiments on bricks	15.02.2019
3.	Results collection, data analysis and final observations	20.02.2019

Language: ……………… **Deadline for submission of thesis:** “…….”………………..201….a

Student: ……………………. ……………………………………“…….”………………..201….a

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ACKNOWLEDGEMENT

Firstly, I would like to thank my supervisor Dr. Can Rüstü Yörük, who has provided support, advice and recommendation during my whole thesis work. I would like to thank Prof. Andres Trikkel for providing an excellent opportunity to carry out the research work in the Laboratory of Inorganic materials.

My special thanks go to the following people and I would like to express my gratitude to all my colleagues for their contribution to this work. I really appreciate the help from Rein Kuusik during the brick molding, Tiina Hain for her assistance in mechanical strength measurements, Mai Uibu for fer help in porosity measurements and Mart Viljus for SEM analysis.

Furthermore, I would like to thank everybody whom I worked within the Laboratory of Inorganic materials for consulting and supporting me in my aspiration.

List of abbreviations and symbols

FA	FLY ASH
BOS	BURNT OIL SHALE
BA	BOTTOM ASH
OS	OIL SHALE
PSD	PARTICLE SIZE DISTRIBUTION
SSA	SPECIFIC SURFACE AREA
XRF	X-RAY FLUORESENCE
XRD	X-RAY DIFFRACTION
TGA	THERMOGRAVIMETRIC ANALYSIS
SEM	SCANNING ELECTRON MICROSCOPE
GHG	GREENHOUSE GASES
CFB	CIRCULATING FLUIDIZED BED
MS	MASS SPECTROSCOPY
TA	THERMAL ANALYSIS
DPS	DUTY PLASMA SEPARATOR

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INTRODUCTION

Ash (bottom or fly) is a by-product of solid fossil fuels (coal, biomass or oil shale) combustion with varying mineralogical, chemical and physical properties, based on the source of the origin of the fuels and on the combustion processes as well. Current ash production in the world is estimated around 600 million tonnes/year where the fly ash (FA) is around 500 million tonnes/year. In this rate, only 20 – 30% are utilized in cement production, bricks and concrete production whereas rest 70% of FA are disposed in landfill and ash lagoons, causing a significant disturbance in the ecosystem [1].

FA disposal is one of the indefatigable process in industry and the main disadvantage of the landfill is that it disperses dust or finer particle from the ground that affects the nearby environment and the top layer gets washed away during rainfall and deposited over the agricultural lands which affects the alkalinity of the soil [2]. With an eye on environmental concern, some countries where the coal is the main source for energy generation and bricks are the main building material, have manipulated a legislation to oblige that if the industry is within 50 km from a coal generation plant then it should utilize at least 25% of FA or BA or PA in the brick manufacturing [3].

The increased global population and immense energy usage result in copious waste generation. Despite concentrated studies on various renewable solutions, none is ready to focus on industrial waste utilization. As an example in the Republic of Estonia, oil shale (OS) industry is the main energy provider which produces about 80% of electricity [4-6] and approximately, 8 million tons of ash is produced every year as the OS has approximately 50% of ash content and thereby the huge ash wastes generated in the power production which becomes a threat to environment due to the alkalinity and trace elements that can accumulate in soil and soil organisms in the long term [7,8].

On other hand, the conventional brick manufacturing sector is facing issues on resource depletion that leads to topsoil erosion and high energy consumption for brick making which makes the to take an incentive action to focus on research of producing green bricks. With the change of habits, the choice of society will change, the demand for sustainable bricks to the conventional one is gradually increasing in nook and corner of the world [9,10].

There are also other types of FA originated from processes such as rice husk waste, agricultural biomass, sawdust, kraft pulp, spent grains, tobacco residue, tea waste, and incineration are also incorporated in fired clay brick manufacturing industry [11,12]. Industrial solid wastes (e.g., coal–wood FA and waste concrete, etc.) are considered as a valuable binder and filling material which can be used in several ways to make the standard processes of cement, concrete and ceramic productions more energy-efficient and environmentally friendly [33].

In this context, in order to reduce the environmental impact of wastes from OS power generation sector, similar concepts towards valorization of the OS ash can be established as one of the applicable options.

Clay brick production with ash additives is a dynamic process with changing raw mixture parameters including complex materials (clay, ash, shale, etc.) which needs to be understood in more detail in the Estonian OS ash context as there has been no research carried out in this field specifically for Estonian OS ashes. This thesis work aims to provide knowledge on the production of FA added clay bricks focusing on two types of FAs (OS ash from Estonia and coal ash from UK) and evaluate their performances in terms of physical, mechanical and thermal properties and to make the knowledge widely available to the fired clay brick and OS sectors, and other building materials manufacturers in Estonia.

As a part of the research activities related to the ongoing project FLAME−FA to valuable minerals (EIT Raw Materials), valorization of OS ashes in clay brick production had been targeted and constitutes the main research topic of this thesis work. The above-mentioned FAs are separated into three different fractions (fine, medium and coarse) using DPS technology and coarse FA is used for brick preparation as they have similar particle size distribution when compared with clay.

The thesis work includes detailed material characterization involving physical, chemical and thermal characterization methods using particle size distribution (PSD), specific surface area (SSA), porosimetry measurements, X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The raw material preparation process includes several activities that took place both in the Laboratory of Inorganic Materials of TalTech and Laboratory of Wienerberger – located in Aseri, Estonia.

Several test and measurements were performed on bricks including dry−wet density, water absorption, flexural and compressive strength, thermal conductivity, image analysis (SEM), FTIR and XRD for mineralogical characterization.

1. LITERATURE REVIEW

Bricks are one of the oldest manufactured products. The main raw material used for brick manufacturing is clay and shale which are obtained from open pits and have a broad composition and varying proportion of silica, alumina, lime and other minerals based in their locality of the soil origination [13]. Clay is a natural earthy fine-grained material that has various mineral commodities, geological occurrence, technology, and application. Clay is adequately plastic to the molding process and on firing clays vitrifies below 1100^{0}C [14]. The wide usage of these materials results in depletion of virgin resources and also the fired clay brick production requires high energy consumption and lead to the cause for high greenhouse gas (GHG) emissions.

1.1 Conventional brick production

The brick production involves pressing moist clay into rectangular molds and drying them under the sun to make sun-dried bricks. The production process and the raw material involved in fired brick manufacturing was not changed from the initial production process that dates to 7000 BC [15]. The conventional process was then developed from hand pressing to machine press where the clay and sand mix is poured into the steel mold and pressed using a hydraulic/pneumatic machine. These wet bricks are stacked up in a loose array, covered with clay or earth, wood fire is developed and maintained for several days [16].

1.1.1 Firing Process

The firing process is the key factor in influencing the properties of fired clay bricks. With respect to the final product, the firing conditions, firing rate and drying time in the kiln differs. The materials gain an irreversible structure after the sintering process and will be responsible for the final properties of the product.

The freshly molded bricks can contain about 25% moisture by weight and usually allowed for drying at room temperature till the moisture level drops to 3 to 15%. Then these bricks are exposed to sintering process where the mechanical moisture is removed at 200^{0}C and at 350^{0}C to 700^{0}C the combustion of innate carbonaceous matter takes place and chemically combined water is evaporated at 400^{0}C to 680^{0}C [63]. At temperature from 600^{0}C to 800^{0}C, calcium carbonate, a common ingredient in the soil gets decomposed to carbon dioxide [17].

$$FeCO_3 \longrightarrow FeO + CO_2 \quad \text{(Temperature, 400 – 700}^0\text{C)} \qquad [1]$$

$MgCO_3 \longrightarrow MgO + CO_2$ (Temperature, 400 – 650^{0}C) [2]

$CaCO_3 \longrightarrow CaO + CO_2$ (Temperature, 600 – 900^{0}C) [3]

$Al_2O_3.2SiO_2.2H_2O \longrightarrow Al_2O_3 + 2SiO_2 + 2H_2O$ (Temperature, 800 – 1100^{0}C) [4]

The development of strength in the brick occurs on the sintering process that causes the clay particles to fuse and progress into strong bonds which are highly stable and resistant to weathering actions and chemical reactions. Mineral phases and liquid phases of $SiO_2 – Al_2O_3$ are formed during the vitrification process, thereby on cooling turns into glass phases and persuades strength to the fired bricks [18,19]. Sedat et al. investigated the effects of firing temperature on compressive strength, water absorption, bending strength, weight loss, firing shrinkage and densities of clay bricks. The specimens were allowed to dry for 24 h initially at room temperature and then muffled to 200^{0}C for 24 h. The firing operations were conducted in an electrical furnace at 700-1100^{0}C in steps of 100^{0}C increment. At this firing condition, above 1000^{0}C, there was an increase in strength, density and firing shrinkage with a decrease in water absorption due to the enhanced vitrification process in the clay materials [20].

In another study, a testing campaign was conducted by Agostino and fellow researchers on quick-firing bricks at moderate temperature to improve mechanical strength. Results indicated that the highest strength is attained at an intermediate firing temperature (800^{0}C) rather than 1000^{0}C and also there was decrease in mass loss during water immersion with reduced moisture buffering capacity [21].

1.1.2 Emissions

The conventional brick manufacturing results in vast consumption of energy as fuel and electricity thereby leading to high economical expenditure. This process causes serious environmental contamination followed by enormous emission of GHG such resulting in smog, acid rain and global warming [22]. In every step of the manufacturing process in bricks, atmospheric emissions such as SO_2, CO_2, NO_x, CH_4, and particulates are produced. This is due to the energy use in raw material transportation and from the kiln combustion [23]. A report on the release of pollutant gases from the raw material emitted from the brick kiln was conducted by Uma et al. From the investigation, it is conveyed that the pollutants emission includes fluorine in the form of stack gases, CO_2 and SO_2. During the sintering process, the hydrogen and fluorine gases are formed and are responsible for acid precipitation. This results in acidification of surface water and leading to tree and crop damage [24].

1.2 Fly ash characterization

FA are the by-product of the combustion of different types of solid fuels from thermal power plants. FAs are generally collected from electrostatic precipitators. The characterization of FA helps to investigate the composition of clayey formulation and gives an overview of the effects of FA addition during the clay-ash mix preparation and final properties of the bricks. FAs has a complex mineralogical composition. This is due to the coal composition, pulverization degree, design of the furnace, combustion process and nature of ash collection [25].

The FA are mainly composed of silica, alumina, and iron oxide with noticeable amounts of Ca, Mg, Na, K, P, Ti, and Mn. These composition of silica, alumina and iron oxide are seen in common clays that are used in the production of fired clay bricks [26]. These compounds presence in FA are determined by the location of energy source, nature of fuel and size of the furnace. These fine particles may exist in the air from a few seconds to several months which are influenced by the particle size distribution of the particulate matter [27].

1.2.1 Fly ash usage in brick manufacturing

The extensive extraction of clay and the use of topsoil consequences to depletion of virgin clay. Researchers have been working on utilizing industrial waste material in place of clay in the brick manufacturing process such that it might reduce the evitable depletion of clay and waste environmental contamination, thereby contributing to a sustainable environment [28,29].

An extensive research was carried out by Fatih and Umit to utilize FA instead of clay in the fired clay brick manufacturing. With incorporation of up to 60% of FA addition, the quality of clay bricks tends to be unaltered. The mechanical strength of FA bricks was increased with a decrease in FA content and increase in temperature [30]. An experimental study of Kayali made a revolution after producing high- performance bricks with 100% FA utilization. These bricks are prepared using the same methods as of conventional brick production. There has been a remarkable improvement in compressive and tensile strength with significant decrease in density of the bricks. It also proved to be more durable and resistant to salt and sulphate attack [31].

1.2.2 Thermal behavior of fly ashes in clay bricks

The thermal characteristics of FA contemplate on their chemical and mineralogical compositions. The endothermic and exothermic reaction of FA at higher temperature can affect the firing conduct of clay-FA mix. A study on Orimulsion FA by Dondi, shows a high weight loss at $1000^{0}C$ that attributed to the thermal decomposition with the release of SO_x from magnesium sulphates, nickel sulphates and a speck from alkaline. The exothermic reaction takes place up to 500^0C with dehydration of sulphates, combustion of carbonaceous component and decomposition of vanadyl sulphates. The endothermic action occurs between 500^0C to 1000^0C that is connected to the decomposition of calcite and magnesite [32]. Another study on coal gasification of FA with clay was experimented by Aineto. It showed two exothermic peaks at 450^0C and 700^0C in thermal DTA curve that are attributed to the oxidation process and development of new mineral phases at high temperature [33].

1.2.3 Firing behavior

A research from Queralt investigated on the firing behavior of clay-FA(60% of clay and 40% of FA) at 900°C and 1200°C. During the temperature range of 900^0C to 1150^0C the vitrification process occurs and all carbonaceous matter gets fully oxidized and the strength of the brick is developed with melting of the clay mass and glassy phase is increased due to amorphization of clay. Above 1150^0C, the kaolinite clays are developed to mullite which causes high mullite content in the material and also the iron-based minerals are converted to hematite. There was also a significant change of color from pale brown to dark brown due to the presence of high oxide content [34].

1.3 Effects of FA on brick property

An investigation on replacement of common clay with 6 wt% Orimulsion FA in the manufacture of fired clay masonry brick was performed by Dondi, Guarini, Raimondo, and Venturi. As FA being hygroscopic, it caused pernicious effects on plasticity and drying rate. Results showed that only 1 to 2 wt% of Orimulsion FA can be used as a partial replacement of common clay as with increase in FA results in decrease in technological properties such as water absorption, thermal conductivity, compressive and flexural strength [32]. In a study from Ananta K Das, where they focused on mixing FA with lime and sand to observe the improvement of brick properties. Their results proved that the optimum properties of bricks can be attained with 30 – 35% sand and 10% lime (70% CaO) content. It was observed that the increase in sand content doesn't affect the water absorption, porosity, and compressive strength to a certain extent but the density and dry weight of the samples became deplorable [35].

With an increase in FA addition in bricks, the binding property gets affected. To demonstrate this, A study from Ranjit Kumar Panda was experimented by adding sodium silicate to FA as a binder. The results show that the compressive strength of FA compacts increased with addition to the sodium silicate and also the microstructure of the particles was dispersed and deviated from their globular equiaxed shape to multifaceted type [36]. Another study on lightweight clay-fly ash bricks samples with different proportion of FA were tested to check the shielding parameters of the bricks. It exhibited that the wall made by clay-FA bricks is adequate for use as a biological protection from perilous radiation as of normal clay bricks. It was explained that these FA bricks can be used as a substitute for pure clay bricks, where space is not a limitation [37].

A study on the addition of higher content of FA in the fired brick production shows that up to 80% of FA can be used as a replacement of conventional clay but the firing temperature is higher than the nominal one. The other main disadvantage is the presence of leachate and radionuclides in brick with high fly ash content where the ash leaching content was higher than European inert limits [38]. Bottom ashes and fly ash were used as the mixtures in the clay brick production. The results show an increase in compressive strength and better ultrasonic pulse velocity compared to conventional clay bricks. It showed an increase in strength up to 30% after the heating process. The optimum ratio of bottom ash, fly ash and clay were found to be 1:1:0.45 which shows better performance of bricks and reveals a good alternative for conventional clay brick [39].

In other study from D.Eliche-Quesada, who investigated the use of coal fly ash in fired clay bricks and silica-calcareous non-fired bricks explained that the increase in the higher amount of ash additive in the production of bricks will results in a decrease of mechanical properties due to an increase in open porosity as well as an increase in water absorption. The increase in porosity is due to the elimination of organic substances and decomposition of carbonaceous matter during the burning process of bricks. It also included in the study that the temperature required to burn the fly ash brick is lower than the conventional clay brick temperature and also the carbon dioxide emissions seem to be lower in the fly ash brick production [42].

Another study on examining the utilization of 20 wt% of FA in the production of fired clay-based bricks was executed by Aineto. This FA additive improves the densification and technical properties of bricks that fired at 900^0C. This effect is explained by the formation of a liquid phase at low firing temperature and also there was slightly darker reddish coloration developed after sintering process [33].

Fly ashes make the brick light in weight and also cost-efficient. In most places, if the brick production industry is around 100 km to a coal power plant then they are incorporated to use at least 25% of fly ash in the brick production [40]. As per the study of Tayfun Cicek and Yasin Cincin, FA bricks produced are solid blocks with the weight per unit volume of 1 t/m3 and while the hollow bricks have a much lower unit volume with better mechanical strength and also the heat conductivity of bricks is superior to the conventional clay bricks [41]. Lingling tested the influence of FA up to 80% in replacement of clay in fired masonry clay bricks. Plasticity property is decreased with an increase in water absorption as they are in line with FA plasticity in nature. Results show a decrease in density and compressive strength of the fired bricks [43].A research on incorporation of electro-static precipitator FA in clay masonry fired bricks were exhibited at 1000^{0}C. Results show an increase in water absorption and reduction in apparent density due to the inert behavior of FA at the firing process. 80 wt% of FA could be added in these bricks whereas maintaining with good technical properties [44].

Baspinar and fellow researchers investigated the use of high sulphate containing fly ash in fired clay brick production with the addition of boric acid (H_3BO_3). The experimental results showed a better clayey formulation at a composition of 10% clay and 5% boric acid with high sulphate containing fly ash, which accelerates the vitrification process due to the reaction of alkali and earth alkali oxides with B_2O_5 [45].

A study on the utilization of FA and steel slag on fired clay brick to determine their influence in technical property behavior was conducted by Bansode. From the results, the addition of 40% FA and steel slag and 60 % clay had a positive influence in water absorption and compressive strength with good clayey formulation, but with the high amount of FA addition, there was a decrease in the adhesive effect of clay [46].An investigation on durability of clay-FA fired bricks was accomplished by Cultrone and sebastin. The results showed an improved durability due to the reduction of small pores in the sintered microstructure of clay bricks. These small pores are in control of the durability of bricks, thereby causes damage to fired bricks due to soluble salt crystallization [47].

1.4 Effects of different FA additives in clay bricks technological property

A study on using FA, sludge and spent grains as an additive in bricks was experimented by Krebs and Mortel [48]. The main objective was to use this waste as an additive for improved porosity in the fired clay brick. The results had improved thermal insulation, less water absorption while maintaining the mechanical strength. Demir investigated the use of processed tea waste in clay bricks manufacturing. 0%, 2.5%, and 5% are varying the mass percentage of waste were used and the results had improved compressive strength and porosity. With a higher amount of tea waste, there was a significant improvement in water absorption, shrinkage and porosity property while the dry density was decreased [49]. Additionally tests were performed on utilizing kraft pulp residues in clay bricks. With the incorporation of 0%, 2.5%, 5% and 10% of residue, there was an increase in water absorption and drying shrinkage with an increased amount of residue. The compressive strength decreased but compiled under the standards. This residue can be effectively used up to 5% in pore forming for the clay [50].

According to Demir, waste such as sawdust, tobacco residues and grass from industrial and agricultural waste can also be utilized in clay brick. With an addition of 2.5% to 10%, the results had increased thermal insulation and plasticity property due to the presence of cellulose fibers [51]. A research was performed by Ducman and Kopar to investigate the effects of addition of sawdust, stone mud, and papermaking sludge waste in different proportion on clay bricks. 30% of sawdust and 100% of silica stone mud were incorporated and fired at 900^{0}C. It was concluded that a combination of sawdust, papermaking sludge and clay produces an adequate strength with higher water absorption [52].

A study on the utilization of coal-mining waste that originated from coal mining and refining process is used in clay brick production. On 5% to 15% of mass addition, there was an improvement in drying behavior and porosity with a decrease in mechanical property of the fired brick. Another research from Dondi et al showed the incorporation of fibrous wool waste and wool wash water treatment sludge in clay bricks was examined. The waste used in the study was about 1.5% to 10%. The results produced a lightweight clay brick with increased water absorption but a lower bending strength [53,54].

Sutcu and Akkurt performed a test using paper processing residues in clay bricks as an organic pore forming additive. 10% to 30% of mass proportion were utilized and fired at 1100^{0}C. Thermal conductivity and porosity were improved on an increase in the inclusion of residues. Therefore, the recycled paper residues act as a pore-forming additive and improvise the insulation property without any changes in mechanical strength [55].Another study on improvising the thermal property and dry density of clay brick using polystyrene were conducted by Veiseh and Yousefi. The mixes contain about 0.5%, 1%, 1.5% and 2% of the mass of the clay. From the results, it could be concluded that with increased amount of polystyrene, the water absorption is increased but the dry density and strength of the manufactured brick is decreased [56].

From these reviews the influence of FA addition to clay bricks can be concluded as following,

- In general, the introduction of FA in a clay body has a positive impact on the thermal and mechanical properties. The clay-FA bricks have varying firing shrinkage, water absorption and porosity, and compressive strength concerning the FA chemical composition.
- The incorporation of FA quantity in clay depends on the nature of clay and FA chemical, physical and mineralogical characteristics.

- In the forming phase, it is important that FA tends to have good mixing properties with clay without reducing the plasticity and shaping characteristics of the raw material. However, FAs are generally not rich in clay minerals mainly includes quartz, carbonates, silicates and mullite particles which have non-plastic property.

1.5 Aim and Scope

The literature review contains valuable information related to the utilization and performance of FAs and other industrial wastes in fired clay bricks manufacturing. Based on the discussed literature data it can be understood that the usage of FAs can create positive impacts in mechanical and thermal properties of fired clay bricks. However, it is a major challenge to be able to control the different clay-FA proportions when there is a new interest of using unconventional ashes like the abundantly produced wastes in the context of Estonian OS.

Thus, there is a necessity to carry out preliminary research on mechanical and thermal characteristics of fired clay bricks and this thesis work aims to provide knowledge on the production of FA added clay bricks focusing on two types of fly ashes–OS ash from Estonia and coal ash from UK (for comparison) and utilized in the replacement of sand in clay-sand mix and evaluate their performances in terms of physical, mechanical and thermal properties and to make the knowledge widely available to the fired clay brick and OS sectors, and other building materials manufacturers in Estonia.

The main objectives to fulfill the defined aim of the thesis work can be listed as follows:

- To obtain knowledge about all materials used in the raw clay - sand - FA mixtures and to carry out detailed material characterization using XRD, PSD and TGA;
- To study thermal behavior and transformations during sintering using thermal analysis (TA) methods and compare thermal properties of pure clay and 20% sand added clay mixtures with BOS and Drax FAs under oxidizing (21%O_2/79%Ar) atmosphere;
- To evaluate typical mechanical and thermal properties of the bricks obtained, run the standard tests and determine their technical physical properties, carry out microstructure analysis using SEM, XRD, etc. and give the respective comparisons;
- To clarify the changes and improvements in the properties related to FA addition and discuss the results.

2 . LITERATURE REVIEW

2.1 Materials and Characterization

Two different types of FAs (named in this thesis work as BOS and Drax) were used for the preparation of FA added clay bricks. The burnt oil shale (BOS) constitutes the main part of the OS residues produced every year in Estonia and collected from electrostatic precipitators of the CFB boilers. The second FA is pulverized coal combustion ash of the Drax coal power plant from the United Kingdom and obtained from the project partner − VITO in "**FLAME**„ (Project - EIT Raw Materials-PA16390). The obtained FA samples had already been separated into different fractions such as coarse, medium and fine using dusty plasma separator technology during the test campaign activities as a part of the project work and coarse fractions were selected for the brick preparations as they had similar particle size distribution on comparison with clay. The clay (Table 1) and sand used in the green shaped bodies were obtained from *Wienerberger Company* − located in Aseri, Estonia.

The material characterization involves physical, chemical and thermal characterization methods using particle size distribution (PSD), specific surface area (SSA), porosimetry, X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Tables 1, 2, 3, 4 and 5 represent the results of all physical and chemical measurements.

Table 1. Chemical composition and some physical properties of clay (Cambrian blue clay)

CaO total (%)	**MgO (%)**	**SiO_2 (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**SO_3 total (%)**	**K_2O (%)**	**Na_2O (%)**	**LOI (%)**	**BET SSA m^2/g**	**Porosity (%)**	**D_{mean}(µm)**
0,4	2,3	61,4	17,8	5,9	1,6	6,1	0,08	4,8	30,86	51,87	15,1

The chemical composition of the clay mostly consists of silica (SiO_2), alumina (Al_2O_3), hematite (Fe_2O_3) and potassium oxide (K_2O). Depending on the type of clay, calcium carbonate or portlandite can also be expressed quite often in the clay matter. However, there is no detected lime content as a chemical constituent in the clay. The loss of ignition (LOI) is 4.8 and the main LOI takes place due to the release of combined water, crystalline water, combustion of organic carbon and oxidation of sulfur.

Depending on the content of carbonates, the release of CO_2 can also play a role in LOI and decomposition of $MgCO_3$ should also be taken into account for this selected clay. The physical properties (density, SSA and PSD) of FAs is represented in Table 2 and 3. The BOS FAs have similar density while the density of Drax FA is slightly lower than BOS FAs. The SSA of Drax FA is 4.4 m^2/g and it is higher than the BOS FAs (~3 m^2/g).

Table 2. Physical properties of BOS and Drax FAs

	BOS coarse	**Drax coarse**	**BOS Initial**
He pycnometry	g/cm^3	g/cm^3	$g/\ cm^3$
Density	2,83	2,28	2,82
BET N_2 sorption	m^2/g	m^2/g	m^2/g
SSA	2,9	4,4	3,0

Table 3. PSD of BOS, Drax and Clay-Sand mixture

BOS coarse		**Bos Initial**		**Drax Coarse**		**Clay + Sand (Reference)**	
Percentiles		Percentiles		Percentiles		Percentiles	
%Tile	Size (µm)	%Tile	Size (µm)	%Tile	Size (µm)	%Tile	Size (µm)
10	11,51	10	3,52	10	7,98	10	3,76
50	29,87	50	33,94	50	22,72	50	11,85
90	59,14	90	108,3	90	42,68	90	58,09

It can be seen from Table 4 and 5, calculated using X-ray diffraction method, the selected FAs have more complex, different chemical and mineralogical compositions with amorphous and crystalline phases. 76.8% of Drax FA and ~28% of BOS FAs are in the amorphous phase. The main differences are in Al_2O_3, SiO_2, CaO, SO_2, $CaSO_4$ contents as well as in silicates (beta − gamma C_2S and mullite) and clay minerals (illite). BOS has higher lime content and fewer silicates compared to the Drax. Most of the silica is in free form as quartz in BOS. There is also more sulfur content in BOS forming anhydrite. The content of illite which is a clay mineral is also less in BOS.

Table 4. Chemical composition and trace elements of BOS and Drax FAs

	BOS Coarse	**BOS Initial**	**Drax Coarse**
Oxides	Wt.%	Wt.%	Wt.%
Al_2O_3	7,46	7,93	21,9
CaO	35,25	33,6	3,22
K_2O	3,32	3,62	2,55
MgO	5,85	5,41	1,6
Mn_2O_3	0,06	0,06	0,1
Na_2O	0,1	0,1	0,97
P_2O_5	0,14	0,15	0,2
SiO_2	31,94	33,95	55,45
TiO_2	0,38	0,4	0,9
SO_3	7,12	6,38	0,23
Na_2O	2,28	2,49	2,64
LOI	4,82	4,62	4,7
SUM	98,72	98,71	94,65
TOC	0,22	0,24	0,32
Trace elements	**mg/kg dm***	**mg/kg dm***	**mg/kg dm***
Zr	44,5	47,1	126
Sr	279	276	477
Cr	39,6	42.9	115
Pb	41	46	50
Ni	24,6	26,7	92,1
Zn	36	38	152
Ba	220	239	1350
V	41,4	46	220

***dm –** Dry matter

Table 5. Mineralogical composition of BOS and Drax FAs

	BOS coarse (cm^2/g)	**BOS Initial (cm^2/g)**	**Drax Coarse (cm^2/g)**
Phase	Wt.%	Wt.%	Wt.%
Quartz	16,1	16,3	9,7
Free Lime	12,6	12,5	7,2
Anhydrite	9,1	8,8	0,5
Calcite	8	8,4	0,7
Periclase	3.8	3,4	2
Hematite	2,9	3	1,7
beta C_2S	2	2	5,3
gamma C_2S	4,4	4,3	5,7
C_4AF	2,1	2,1	3,4
Mullite	0	0	7,5
Magnetite	0	0	2,8
Ca-langbeinite	2,5	2,5	3,2
Orthoclase	4,5	5,2	6,6
Illite	3,6	3,8	6,5
Amorphous	28,3	27,6	76,8

Thermogravimetric Analysis

For TGA analysis, Seteram labsys Evo 1600 thermoanalyzer coupled with Pfeiffer Omnistar mass spectrometry (MS) by a heated transfer line was used under non-isothermal (10K/min) conditions up to 1025^0C. It is widely used for in-depth analysis of thermal behaviors or phase transitions like melting, crystallization, glass transition or reactions like curing and oxidation of the materials. Standard alumina (Al_2O_3) crucible was used and oxidizing (21%O_2/79%Ar) atmosphere was selected. TG-MS results are represented in the following figures 1(a,b), 2 and 3 for BOS, Drax, pure clay and 80% clay - 20% sand mixtures respectively.

First mass loss step of both FAs is water evaporation and as the samples tested without pre-drying (as received) the content of physical bonded water can be bigger than as it was collected from power plants.

After water evaporation BOS sample has two more typical distinctive mass loss steps; first is the $Ca(OH)_2$ decomposition and the second one is mainly dolomite and $CaCO_3$ decomposition.

Drax has also one additional mass loss step after water evaporation and can be related to the oxidation of unburnt carbon and pyrite as there are two exothermic peaks on the DTA curve (Fig.1).

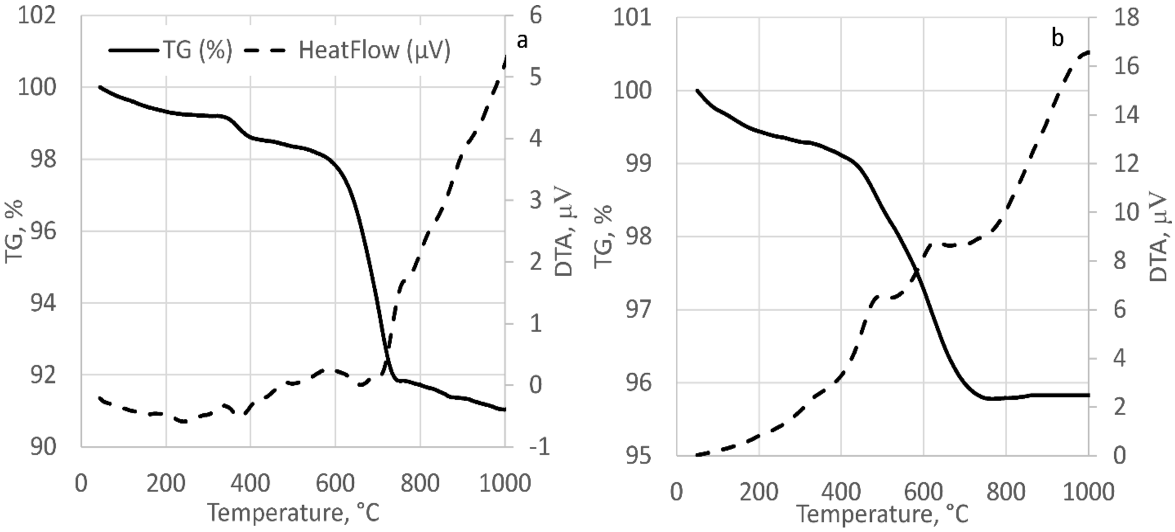

Figure 1. TG-DTA curves of BOS(a) and Drax(b)

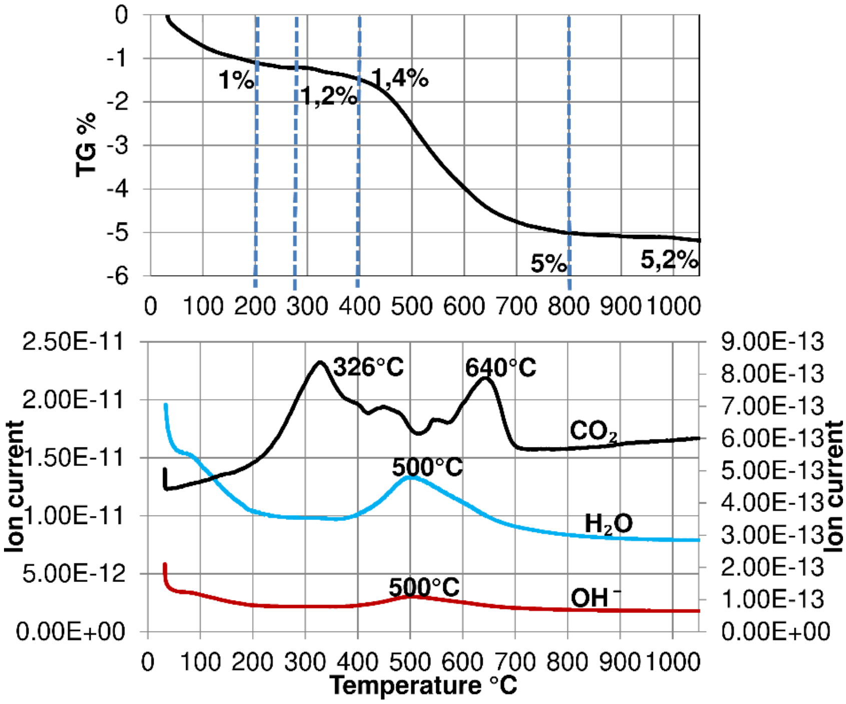

Figure 2. TG curve of clay (above) and CO_2, H_2O and OH^- spectra (below)

First mass loss step (Fig. 2) is related to the emission of hygroscopic water (1%) which has prolonged evaporation up to 200°C and later there is an emission of crystal water which is related to the dehydration of gypsum between 200-300°C. There is a small amount of organic matter and it is thermooxidized between 300-400°C (CO_2 emission profile peak 326°C).

The early stage dehydroxylation of illite, illite-smectite, mica, kaolin are started after this temperature range and prolongs up to 700°C. Further release of CO_2 emissions can be related to the decomposition of carbonates mainly $MgCO_3$ according to the XRD (Table 1). Similar processes take place also in the 80% clay - 20% sand mixture just resulting in less LOI due to the sand addition.

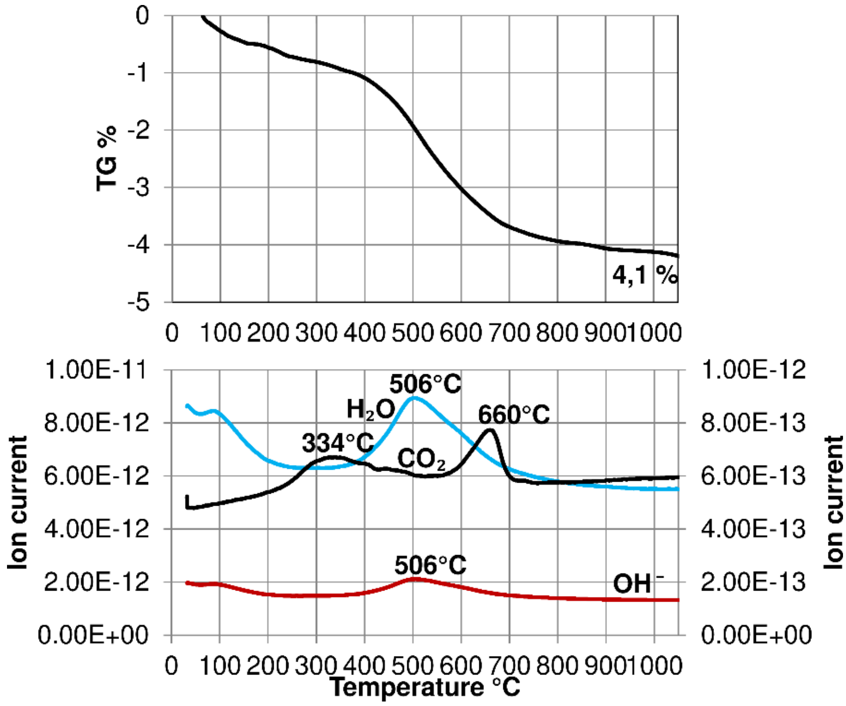

Figure 3. TG curve of 80% clay – 20% sand (above) and CO_2, H_2O and OH^- spectra (below)

2.2 Raw material Preparation and Molding of Bricks

In total, 12 handmade brick bodies were prepared. A reference brick was prepared with a mixture ratio of 80% clay – 20% sand. A constant proportion of 80% clay – 10% and sand – 10% FA was followed for the FA added bricks for the whole sampling process. The raw material preparation process includes several activities that took place both in the Laboratory of Inorganic Materials of TalTech and Laboratory of Wienerberger – located in Aseri, Estonia.

Firstly, the obtained fresh clay was dried then hardened junks were broken down using a big ball mill for 20 minutes to obtain material in smaller particle size. Subsequently, clay was grounded to a fine powder using a four-ball planetary mill (clockwise rotation for 10 minutes at 350 rpm, anti-clockwise rotation for 5 min at 350 rpm) and dried at 105^{0}C for 4 hours. Later, raw materials were mixed in certain ratios and water ratio was fixed to obtain similar plasticity behavior of the mixtures. An infrared moisture analyzer was used to measure the water content of the mixtures. For BOS bricks 20 wt% water was used while for Drax and Reference bricks 15 wt% water was used. The water ratio of BOS bricks was slightly higher to obtain similar plastic behavior of the raw mixtures.

Prepared mixtures were poured into the prisms 40 x 40 x 160 (mm) (Fig.4) according to EN 196 and ISO 679, later hydraulic press (Fig.2.4) was used to develop an equal amount of pressure over the mold that was kept 10 seconds and exactly 75 kg/cm^2 pressure was applied (Table 2.6).

Table 6. Sampling process

Sample Names	Content (%) Clay + Sand +Ash	Water Ratio (%)	Pressure (kg/cm^2)
Reference	80+20+0	15	75
Drax	80+10+10	15	15
BOS Initial	80+10+10	20	75
BOS Coarse	80+10+10	20	75

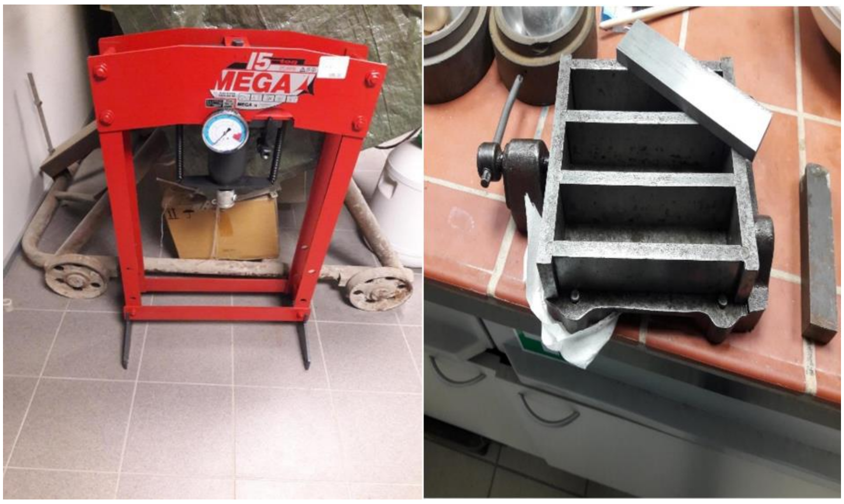

Figure 4. Pictures of hydraulic press and cuboid mold

The prepared green bodies were left drying after molding; first at room temperature (12 hours) then in drying chamber (with slow temperature ramps up to 105^0C) until water evaporation related mass change stops before transferring them to the sintering stage. This process was carried out to avoid possible swelling or bloating of the samples at high temperature, caused by the expansion of entrapped water. Then the samples were sintered at $1025^{\mathbf{0}}$C which took approximately 48 hours (including slow heating and cooling cycle) in an industrial tunnel furnace of Wienerberger under oxidizing conditions.

2.3 Tests and Measurements

Dry and Wet Density

After press molding, the samples were weighted down and dimensions were measured to determine the wet density. The same process was repeated after drying and sintering to obtain both dry density and end product density values.

Water Absorption

The water absorption test involves soaking of bricks for 24 hours according to the EN 771-1:2003 [59]. The bricks were immersed in the water for 24 hours at a temperature of 23 ± 2^0C. The samples are weighted down to determine the percentage of water absorption.

Flexural Strength

Flexural strength test determines the maximum bending stress of bricks before it yields. This test was conducted on TONI TECHNIK D-13355 Berlin model (Fig.5) which works in accordance with EN ISO 7500-1 with prisms 40 x 40 x 160 (mm).

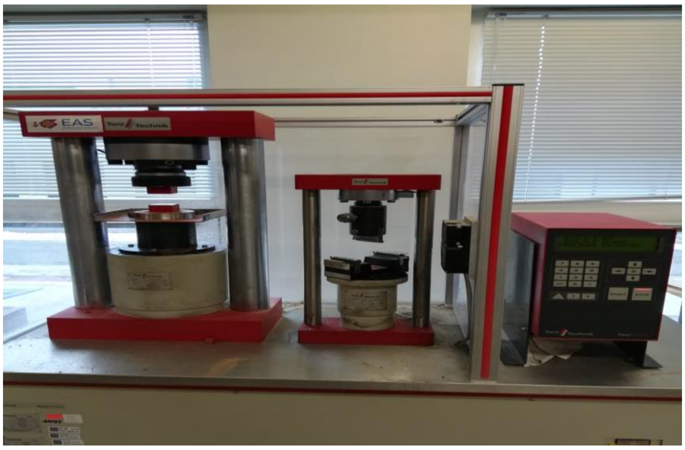

Figure 5. Compressive and Flexural strength test equipment

Compressive Strength

The compressive strength test was performed in accordance with EN 196 and ISO 679 [60]. The broken bricks from the flexural strength test were used for the compressive strength measurements. This test was carried out in the same apparatus which applies progressing load at the rate of 0.7 kN/sec.

Thermal Conductivity Test

This test was carried out with HOT DISK TPS 2200 instrument which meets the ISO 22007-2 standard [61]. The broken samples from the flexural strength were used for this analysis. The hot disk Teflon sensor was placed in between the joints of the broken pieces and the thermal conductivity was measured at a rate of 10 Kelvin/second. The experiment is repeated on different sides of the same bricks and the mean value was determined for further calculation.

Porosity test

This test was carried out with POREMASTER PV007130 which uses automatic mercury intrusion for pore size analysis and works on accordance with ISO 9000 standard [62]. Measurements were focused on intraparticle porosity which is the porosity within individual grains or particles and total porosity was also measured in order to investigate all void spaces regardless of interconnected or isolated pores.

SEM and XRD analysis

In order to investigate the microstructure and mineralogical composition of the sintered bricks SEM images were obtained from the polished samples using ZEIS Evo MA 15 and XRD analysis was ordered from Tartu University for Reference, BOS and Drax added bricks.

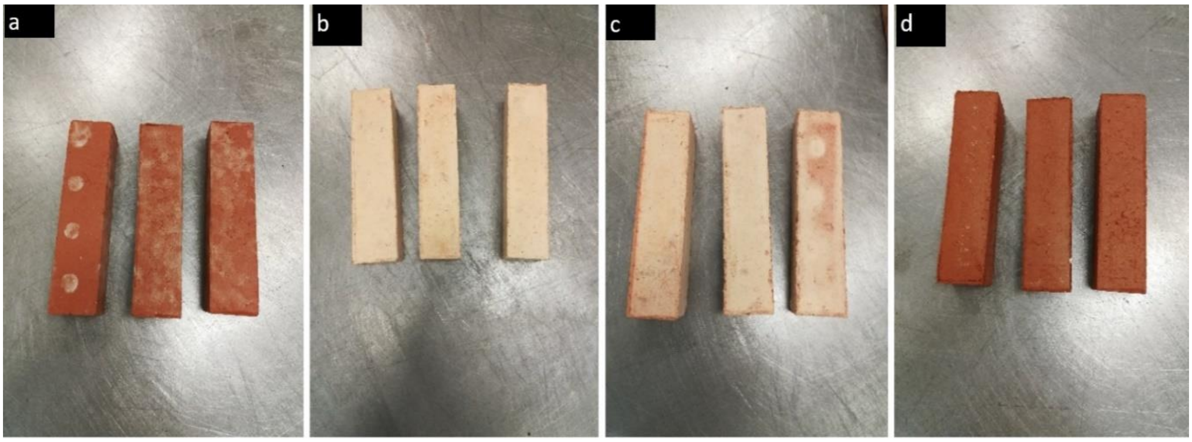

Figure 6. a) Drax b) BOS Coarse c) BOS Initial d) Reference

3 RESULTS AND DISCUSSION

3.1 Dry and Wet Density

The densities of bricks after molding, drying and sintering are presented in the Table 7. Dry densities are lower when they are compared with wet densities and values are proportional to the initial water ratio of the Reference and Drax bricks. However, the possible reaction between free CaO and water bonds the water chemically in the case BOS added bricks that's why the dry density is not proportional to preliminary water ratio of the raw mixture. It can also be seen that the values of Reference and Drax bricks show increased density after firing while the density of BOS bricks is slightly decreased.

Table 7. Dry density, wet density, and density after firing results

(Average Values)	Reference	Drax	BOS Initial	BOS Coarse
Wet Density (kg/m^3)	2264	2198	1868	1818
Dry Density (kg/m^3)	1937	1887	1779	1744
Density After Firing (kg/m^3)	2107	2186	1723	1766

3.2 Shrinkage Property

The shrinkage of bricks after drying and sintering was given in (Table 8) which shows the comparison with the volume of samples before and after the molding and sintering processes. From the results, it can be noted that the reference bricks have the highest shrinkage after drying and Drax bricks have the highest shrinkage after sintering. The main changes suffered from the fired FA-clay bricks dry density is due to the mineralogical evolution that occurs during the drying period at room temperature and firing process explains the inherent property of FA which accompanies with the volume reduction. The initial drying shrinkage is dependent on the amount of drying period of the wet brick from the casting process. From the addition of FA in the brick, a notable reduction of shrinkage after the drying and sintering process can be observed.

Table 8. Shrinkage after drying and sintering

Average Values	Reference	Drax	Bos Initial	Bos Coarse
Shrinkage after drying (%)	7	6	4	5
Shrinkage after sintering (%)	11	16	5	6

3.3 Water Absorption

It is shown (Table 9) that the BOS bricks have the highest water absorption values and Drax comes second and later Reference bricks which have the lowest water absorption. This can be explained with the degree of compactness and porous structure of the bricks simply indicating the early sign of higher porosity in the BOS bricks, which leads to an increase in water absorption value (2.5 times) when compared to the Drax and Reference bricks.

Table 9. Water absorption test

Samples	Drax	Reference	BOS Initial	BOS Coarse
Water Absorption Avg. (%)	5,72	5,13	13,91	13,31

3.4 Compressive and Flexural Strength Test

The measurement of compressive strength is important in order to determine the load carrying capacity of bricks under compression. Depending on the increase in the porosity ratios of BOS bricks, it can be expected to see somewhat decrease in compressive strength values of the BOS bricks. However, the measured strengths are still comparable with Drax bricks and slightly higher than Reference bricks. The obtained average value for the compressive strength of Drax is 27% higher than the Reference bricks, 16% higher than the BOS initial brick and 10% higher than the BOS coarse bricks. Flexural strengths are also necessary to estimate the wall resistance when exposed to lateral loads (like wind, earthquake).

The average value of Drax bricks is 67% higher than the Reference bricks, while average values of BOS bricks have approximately 30% less flexural strength than Reference bricks (Table 10).

Table 10. Compressive and Flexural strength test

Samples	Compressive Strength, First (MPa)	Compressive Strength, Second (MPa)	Flexural Strength (MPa)
Drax 1	23,65	27,01	11,82
Drax 2	_*	_*	11,75
Drax 3	19,73	23,14	7,86
Drax Avg,	21,69	25,07	10,47
Ref. 1	_*	_*	6,34
Ref. 2	18,91	16,97	6,52
Ref. 3	18,36	19,09	5,94
Ref. Avg.	18,63	18,03	6,26
BOS – Initial 1	20,37	21,81	4,51
BOS – Initial 2	26,35	18,98	3,67
BOS – Initial 3	20,16	20,66	4,55
BOS Avg.	22,29	20,48	4,24
BOS – Coarse 1	18,81	18,65	4,39
BOS – Coarse 2	18,01	21,24	5,40
BOS – Coarse 3	_*	_*	3,45
BOS Coarse Avg.	18,41	19,94	4,41

*Deviation above 30%

3.5 Thermal Conductivity

To determine the thermal conductivity of the prepared bricks, rapid thermal conductivity measurement with a hot disk sensor was used on broken samples from the flexural strength tests. From the measured thermal conductivity values of the fired FA bricks, given in table 11, BOS bricks have gained reasonably good thermal insulation character and values decreased by up to 50% compared to the Reference bricks while adequate mechanical strength could be maintained. It can also be observed that thermal conductivity varies depending on the porosity and conductivity of solid and also exhibits a decrease in trend with bulk density.

Table 11. Thermal Conductivity test

Samples	Drax	Ref	BOS Initial	BOS Coarse
Thermal Conductivity Avg. W/m.K	1,17	1,25	0,67	0,71

3.6 Porosity

An overall porosity reduction is expected at when the vitreous phase fills the pores during the firing process which reached above 1000°C. From the porosity results shown in Figure 7 and Table 12, it is depicted that the BOS added samples show a higher concentration of intraparticle pore features in the range of 0-4 µm when compared with other samples and include pores above 3 µm. Total porosity is approximately 2 times higher in BOS added samples. These results show that the formulation of denser well-sintered microstructure can be maintained and even improved with Drax ash and BOS can be used as pore-forming additives since the further increase in the concentration of ash in brick bodies could make the bricks mechanically weak due to the higher concentration of calcite which decomposes at high temperatures and leaves rims of empty space [57].

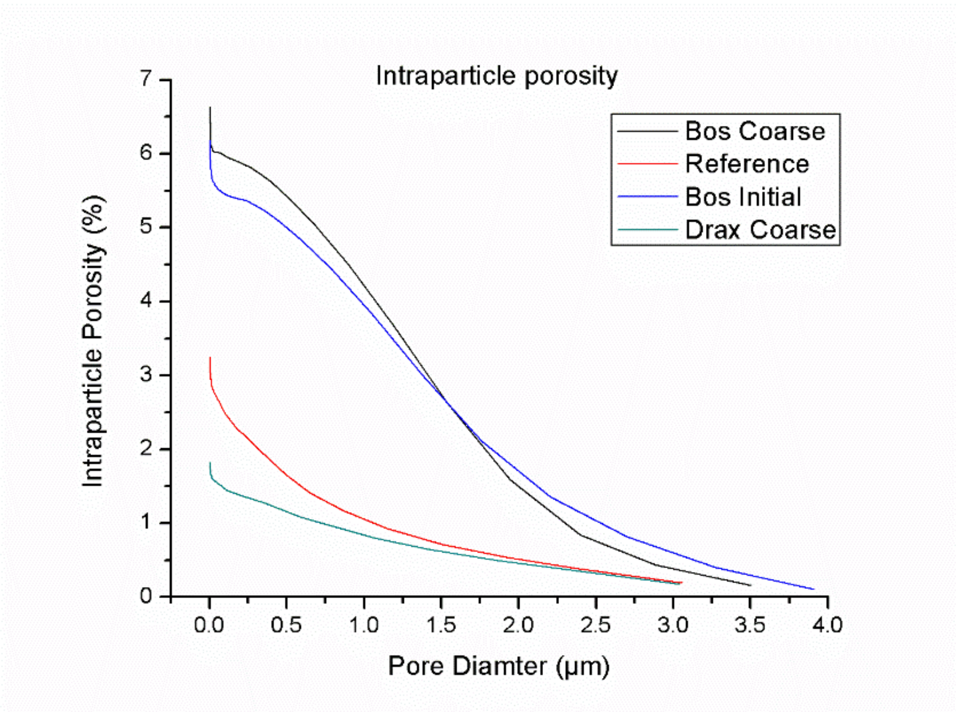

Figure 7. Intraparticle porosity of bricks

Table 12. Total porosity of bricks

Sample name	Total Porosity (%)
Bos initial	9,765
BOS coarse	8,154
Drax coarse	4,049
Reference brick	5,855

3.7 SEM Analysis

The SEM images of the brick samples are shown in figures 8-9. It can be seen that the presence or absence of carbonates strongly influences the porosity development and therefore, the brick texture and as a result, physical-mechanical properties are also influenced. A higher degree of particle interlocking can be observed from reference and Drax added samples which result in a porosity reduction due to undisturbed melting of clay particles in the matrix. BOS samples with higher carbonate content which undergo different mineralogical changes give an interesting picture of local phase transformations taking place at grain boundaries which allows easy detection of the porosity increase.

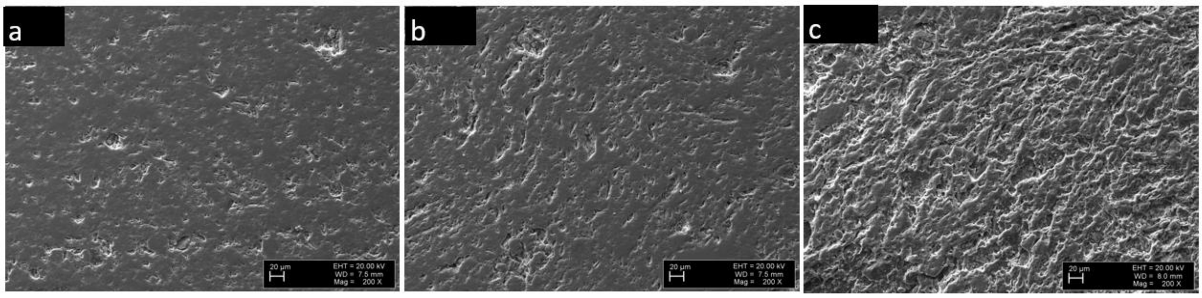

Figure 8. SEM 200x a) Reference brick b) Drax FA added brick c) BOS FA added brick

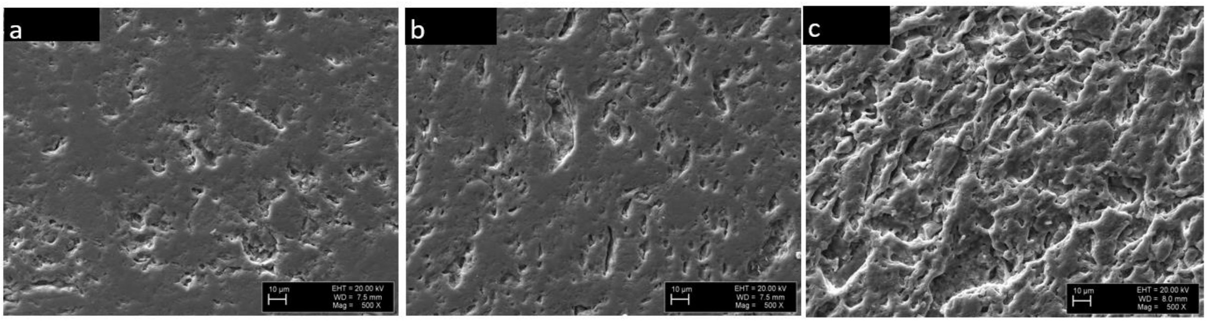

Figure 9. SEM 500x a) Reference brick b) Drax FA added brick c) BOS FA added brick

3.8 XRD test of fired bricks

It is clear that the mineralogy of the bricks, as well as the mineral transformations, taking place upon firing and there are differences in the contents of feldspar minerals like K-feldspar and plagioclase depending on the initial chemical composition of the materials (Table 13). BOS added sample has more plagioclase and K-feldspar and has less quartz content compared to other samples. A high percentage of calcium carbonate in the clay material may cause lime flaking in the fired bricks, and may produce a scum of white calcium sulphate on the exposed surfaces of the fired bricks, especially when a significant amount of SO_2 is released from the fuel during firing [58]. According to the XRD results it can be seen that the content of anhydrite ($CaSO_4$) is higher in BOS added bricks and this might explain the pale yellowish color of the BOS added bricks. Formation and transformation of new material structures are also clear by looking at the non-carbonate inorganic materials forming spinel and mullite in FA added bricks and replacement of sanidine.

Table 13. Mineralogical composition of bricks

	Quartz (cm^2/g)	**K-Daystone (cm^2/g)**	**Plagio-class (cm^2/g)**	**Mica (cm^2/g)**	**Hematite (cm^2/g)**	**Anhydrite (cm^2/g)**	**C2S/C4AF (cm^2/g)**	**Sanidine (cm^2/g)**	**Spinel (cm^2/g)**	**Mullite (cm^2/g)**
Ref.	58,04	12,68	-	3,60	3,87	-	-	9,79	11,80	-
BOS	31,30	20,89	17,38	6,03	4,56	2,14	1,80	-	10,21	3,71
Drax	43,71	16,27	3,46	4,38	5,40	0,99	-	-	18,41	6,31

4 CONCLUSIONS

Two different types of FAs (BOS and Drax) were used for the preparation of FA added clay bricks. The effect of FA addition were investigated in terms of mechanical and thermal properties of the bricks.

From the specific findings on the experimental investigations of FA added bricks the following conclusions can be drawn out;

- Physical, mechanical and thermal properties (i.e., water absorption, color, texture, density, porosity, strength, and thermal conductivity) of prepared bricks are affected by the different composition of the raw materials used in each green bodies.
- Color of the bricks changes with the addition of FAs. The BOS addition causes a shift from darker to lighter colors after firing, which can be explained with the formation of $CaSO_4$ and greater the concentration of BOS in bricks greater the shift in color can occur gradually.
- End product density values of Drax and Reference bricks are increased after the sintering process. However, BOS bricks have slightly decreasing density values which can be due to the effect of $CaCO_3$ decomposition at high sintering temperature and resulting presence of higher porosity.
- The decrease in density and intraparticle porosity of Drax bricks can be correlated with their increase in strength and lower water absorption.
- According to the observed average compressive and flexural strengths, it is comprehended that the bricks and the masonry can strongly resist the compressive stress than the flexural. Drax bricks have the highest flexural and compressive strength due to the increased composition of minerals like illite, beta−gamma C2S, mullite and specifically high contents of aluminum-oxide and quartz which are thermally transferred to glassy phase during the vitrification process.
- At ambient condition, the effective conductivity of the material varies with respect to the porosity ratio and BOS FAs has the lowest thermal conductivity which shows that bricks including BOS can act as an insulator. This exquisite result from BOS sample is related to the increased porosity in the microstructure.

Consequently, all results indicate that both BOS and Drax FAs could be easily utilized in clay-based brick bodies as pore-forming additives in order to lower the thermal conductivity and to increase the strength, respectively. BOS added bricks have gained reasonable thermal insulation character while adequate mechanical strength could be maintained. This preliminary work highlights a tremendous lack of locally relevant research on this very important construction material. Based on the promising study results obtained in this thesis work, the study of addition of FAs into clay brick bodies requires further investigation to make the end products more marketable with more promising mechanical and thermal properties. Future research can target to the preparation of bricks in a higher concentration of FAs and further life cycle assessments tools can be used for possible environmental aspects. In case of successful outcomes from the relevant R&D, FA utilization in clay-based bricks can be a propitious solution for the OS based energy sector of Estonia as a new alternative way for recycling FA wastes to solve part of solid waste disposal problem with the cost-saving methods.

SUMMARY

Oil shale (OS) is Estonia's primary fossil fuel resource and it almost meets the energy needs independently. Approximately 80% of the electricity consumed is generated from OS. Despite the energy supply, there is a challenge of using OS due to a large amount of ash produced every year, where the majority of them are disposed in landfills and only a minimal quantity is utilized (~2%) in construction and agriculture sectors. There is a growing landfill space demand for these alkaline hastes as they are not efficiently used and stabilized in different industries.

In this context, in order to reduce the environmental impact of wastes from OS power generation sector, similar concepts towards valorization of the OS ash can be established as one of the applicable options. As a part of the research activities of thesis work which is also related to the ongoing project FLAME−Fly ash to valuable minerals (EIT Raw Materials), valorization of OS ashes in clay brick production had been targeted. This thesis work aims to provide knowledge on the production of fly ash (FA)added clay bricks focusing on two types of FA (OS ash from Estonia and coal ash from UK) and evaluate their performances in terms of physical, mechanical and thermal properties and to make the knowledge widely available to the fired clay brick and OS sectors, and other building materials manufacturers in Estonia.

The material characterization part of the thesis work involves physical, chemical and thermal characterization methods using particle size distribution (PSD), specific surface area (SSA), porosimetry, X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). The raw material preparation process includes several activities that took place both in the Laboratory of Inorganic Materials of TalTech, Laboratory of Wienerberger – located in Azeri, Estonia and separation of different fraction of FA in VITO.

Additionally, several tests and measurements were performed on bricks including dry−wet density, water absorption, flexural and compressive strength, thermal conductivity, image analysis (SEM), and XRD for mineralogical characterization. All results indicate that both selected OS shale ashes and coal ash could be easily utilized in clay-based brick bodies as pore-forming additives in order to lower the thermal conductivity and to increase the strength, respectively. Thus, this thesis work concludes that studied and similar type of ashes could be used in the production of valuable construction materials as clay-based bricks. This new alternative way of utilization can solve part of solid waste disposal problems by reusing them in brick bodies and can also be a cost-saving methodology by limiting the usage of raw materials (sand, clay, shale etc.).

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