



# Alkali activated construction materials: Assessing the alternative use for oil shale processing solid wastes



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## HIGHLIGHTS

- Additional source of silicate is needed to achieve polymerization.
- Main reaction product responsible for structural strength is a C-(A)-S-H phase.
- Structure and formation of C-(A)-S-H phase is limited by reactive Ca bearing phases.
- C-(A)-S-H gel is predominantly a depolymerized one dimensional structure.

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## ABSTRACT

The potential of oil shale ash wastes as a source material for geopolymeric or alkali activated construction materials was assessed using structural, XRD, SEM, SEM-EDX, ATR-FTIR and <sup>29</sup>Si MAS-NMR methods. Fresh, unhydrated furnace bottom and cyclone separator ash along ash plateau sediment were used in combination with 5 M NaOH and Na<sub>2</sub>SiO<sub>3</sub> solutions with SiO<sub>2</sub>/Na<sub>2</sub>O ratios of 2.72 and 1.5 as alkaline activators, under ambient curing conditions. Our analytical results show that only activator solutions containing soluble silicate will induce the formation of amorphous C-(A)-S-H gel, giving the samples 8 times higher compressive strength (8.5 MPa) than samples exhibiting cementitious properties upon hydration (1.25 MPa).

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## 1. Introduction

Oil shales are low quality fossil fuels that can be pyrolyzed to extract shale oil or burn in thermal power plants to produce heat and electricity. Oil shale sedimentary deposits that are both marine or lacustrine in origin are found all over the world, but their industrial scale usage is limited to few countries including Brazil, China, Estonia, Jordan and Israel, mainly because of low calorific values, and technological and environmental issues. However, ever growing demand for energy resources has created interest in exploiting oil shale reserves in Green River Formation in USA [1], Huadian deposits in China [2], Jordan's oil shale [3], and Queensland deposits in Australia [4].

Kukersite oil shale that has been mined in Estonia for nearly 100 years is composed of organic, carbonate and terrigenous

material in various proportions [5]. The content of organic matter varies between 10% and 60% and is mostly composed of kerogen, but also contains few per cent of bitumen. Processing of oil shale leaves more than 50% of solid waste (ash), which has a limited secondary usage. The annual oil shale mining output in past five years has been at the level of 12–15 Mt and about 80% of mined oil shale is burned in thermal power plants for electricity and heat generation using pulverized fuel (PF) or circulating fluidized bed (CFBC) combustion technologies with temperatures reaching about 1300 °C and 700–850 °C, respectively [6]. As a result, in 2014 ca. 7.5 Mt of ash formed at Estonian thermal power plants.

Oil shale ash is a light-colored mineral material that is composed of lime, calcite, anhydrate, different secondary Ca-silicate phases and residual non-carbonate fraction in varying proportions. Composition of the waste depends on processing technology and raw oil shale composition, but the remaining ash is most commonly Ca-rich with CaO content as high as 55% [7]. By its composition oil shale ash is most similar to type C fly ash from coal combustion. Although oil shale ash has to some extent been used

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as a constituent in cement, in road construction and for agricultural purposes [8,9] or filter material [10–13] the reuse is minimal and most of it (ca. 95%) becomes deposited in large ash fields next to power plants. The higher concentrations of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and lower CaO and LOI values of electrostatic precipitator ash fraction, compared with other oil shale processing solid wastes, allow it to be used as an additive in ordinary Portland cement [9,14] that accounts for the largest part of the reuse of oil shale ash, but all other ash fractions from the power plants are not used in any beneficiary ways and become hydraulically transported in slurry with a water-to-ash ratio of 20:1 to sedimentation ponds, where it solidifies [7,15] and up to 50 m high stabilized ash plateaus with steep slopes have formed. The plateaus occupy an area more than 20 km<sup>2</sup> and accommodate more than 300 Mt of ash [15]. The structural, chemical, mineralogical and physical properties (as well as cementation) of oil shale ash have been thoroughly studied and presented in last decades (e.g. [7,14–19]), but secondary use of the oil shale ash has stayed limited, partly due to the lack of suitable alternative applications.

Production of geopolymeric binders by alkali activation of waste materials as an alternative to common Portland cement by depolymerization and subsequent repolymerization of aluminosilicate structures in alkaline medium, is a rapidly growing field in building materials research. This technology enables more efficient reuse of different solid waste types including combustion ash, metallurgical slag or glass processing wastes [20]. It is also important that using industrial by-products as the source materials for construction materials the carbon footprint and energy consumption of the production process could be significantly reduced [21]. The industrial by-products used to produce alkali activated materials (AAM) are mainly low calcium varieties of blast furnace slag and coal fly ash [22,23]. Depending on the raw materials and activation conditions, geopolymeric AAM-s may exhibit different properties necessary for specific applications such as: high compressive strength, acid and/or fire resistance, low thermal conductivity etc. While low calcium (class F) fly ash is most commonly used for synthesis of geopolymeric materials, also high calcium (class C) fly ash use has been evaluated [24–26]. In this contribution we study the potential of different Ca-rich oil shale industrial solid waste types produced in Estonian thermal power plants for AAM type mortar and cement production as an alternative for its secondary beneficial use. Reinik et al. [27,28] have previously shown that hydrothermal alkaline (NaOH and KOH) treatment of oil shale ash at high temperatures produces Al-substituted tobermorite, the important constituents of concrete [29], but up to our knowledge the geopolymeric potential of oil shale ashes for construction applications and alkaline activation under ambient conditions has not been studied before.

## 2. Material and methods

### 2.1. Ash materials

Fresh ash materials used in this study were derived from Balti Thermal Power Plant that uses oil shale as the primary fuel. In addition, the hydrated ash from ash depositories at the same power plant was sampled. Fresh, unhydrated furnace bottom (BA) and cyclone separator (CA) ash materials were obtained from the ash separation system at a boiler operating on pulverized firing technology. The hydrated ash plateau sediment (APS) was collected from about 1.5 m deep trench excavated on the ash depository.

### 2.2. Experimental design and sample preparation

Four different series of mixtures were prepared with each ash material type (Table 1). All activation solutions were prepared freshly before the mixing. Directly after mixing, the fresh paste was poured into 40 mm-high and 40 mm-diameter cylindrical moulds and placed on a vibrating plate for 1 min. The mixing was performed in laboratory environment at average ambient temperature of 22 °C and relative humidity 50–55%. The samples were then left to cure under the same

**Table 1**

Mix designs of samples used in the study. SiO<sub>2</sub>/Na<sub>2</sub>O and Na<sub>2</sub>O values represent the alkali activator components and not the overall chemical composition of the mixtures. APS - ash plateau sediment, BA - bottom ash, CA - cyclone separator ash.

Mixture	Water/ash	Na <sub>2</sub> O/ash	SiO <sub>2</sub> /Na <sub>2</sub> O
CA H <sub>2</sub> O	0.5		
CA NaOH	0.5	0.09	
CA 2.72 M Na <sub>2</sub> SiO <sub>3</sub>	0.5	0.1	2.72
CA 1.5 M Na <sub>2</sub> SiO <sub>3</sub>	0.5	0.1	1.5
BA H <sub>2</sub> O	0.45		
BA NaOH	0.45	0.08	
BA 2.72 M Na <sub>2</sub> SiO <sub>3</sub>	0.45	0.1	2.72
BA 1.5 M Na <sub>2</sub> SiO <sub>3</sub>	0.45	0.1	1.5
APS H <sub>2</sub> O	0.7		
APS NaOH	0.7	0.13	
APS 2.72 M Na <sub>2</sub> SiO <sub>3</sub>	0.7	0.1	2.72
APS 1.5 M Na <sub>2</sub> SiO <sub>3</sub>	0.7	0.1	1.5

conditions in open air environment for 7 and 28 days. The water binding capacities of each material type derived under pore space saturation conditions were determined experimentally before preparation of mixtures and the corresponding ratios were used in the mix design to ensure full reactivity and maximal dissolution of the silicate phases present in the solid wastes.

The oil shale ash waste materials exhibit cementitious properties upon hydration and mixtures with water were first prepared as the reference to determine the degree of polymerization reactions in alkaline medium. The second series of test samples was prepared using a NaOH solution. A 5 M NaOH solution was used to prevent the formation of ettringite which would significantly affect the strength of the material. Ettringite is a common and abundant phase in hydrated oil shale ash [30]. The third series was prepared using a commercial sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>) solution with SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 2.72 and water content of 47.4% (w/w). The fourth series was prepared using a sodium silicate solution in which the molar ratio of SiO<sub>2</sub>/Na<sub>2</sub>O was modified to 1.5 by NaOH addition as suggested by Duxson et al. [31] [32]. All sodium silicate based activator solutions were adjusted so the Na<sub>2</sub>O concentration in the additive was 10% (w/w).

### 2.3. Analytical methods

Uniaxial compressive strength of the materials as an initial indicator of the geopolymerization reactions was measured under continuous loading (20 kPa s<sup>-1</sup>) until the specimen broke. Compressive strength was measured in three replicas after 7 and 28 days of curing.

Mineral composition of the test samples and original ash materials was determined using X-ray diffraction analysis. Ground and homogenized randomly oriented powder samples were measured on a Bruker D8 diffractometer using Ni-filtered CuK $\alpha$  radiation and LynxEye linear detector over the 2–70 °2 $\theta$  region. Quantitative mineral composition of the samples was interpreted and modelled using Rietveld algorithm based code Topaz 4.0.

Chemical composition of the ash materials was determined by means of X-ray fluorescence spectrometry on Rigaku Primus II XRF spectrometer using SQX quantification model. The thermogravimetric (TGA) and differential thermal analysis (DTA) of raw materials was performed on STA 449 F3 Jupiter thermal analyzer in Al<sub>2</sub>O<sub>3</sub> crucibles by heating to 1000 °C at 10 °C/min. The microstructure and chemical composition of the mixtures were investigated using Zeiss EVO15MA SEM with Oxford X-MAX energy dispersive detector. Attenuated Total Reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) patterns of geopolymerized pastes were measured using a “Smart Orbit” diamond ATR-microanalyser attached to Thermo Scientific Nicolet 6700 FT-IR spectrometer with Csl optics and DLATGS detector. Transmittance IR spectra were collected from 225 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with 128 scans per sample. Formation of amorphous calcium-silicate-hydrate (C-S-H) complexes in CA mixtures after 28 days of curing were estimated using <sup>29</sup>Si magic angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR) at <sup>29</sup>Si resonance frequency 71.4 MHz on Bruker AVANCE-II NMR spectrometer attached to 8.5 T magnet. About 1.5 g of sample was rotated at 5 kHz in 10 mm zirconia rotors using home built MAS probe.

## 3. Results and discussion

### 3.1. X-ray diffraction and thermal analysis

Chemical and mineralogical composition of the initial and treated ash materials are shown in Tables 2 and 3, and Figs. 1 and 2. Fresh, unhydrated, BA and CA ash contain lime, portlandite, anhydrite, calcite, quartz and secondary Ca-silicates. Most abundant reactive Ca-phases are belite/C2S (Ca<sub>2</sub>SiO<sub>4</sub>) and lime (CaO<sub>free</sub>)

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