

ALKALI ACTIVATION OF ESTONIAN CA-RICH OIL SHALE ASHES: A SYNTHESIS

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Abstract. *This contribution reviews the geopolymeric potential of Ca-rich oil shale processing residues and aims at the characterization of the effects of different alkaline activator solutions on the polymerization of oil shale processing residues experimentally tested in recent-case studies. The analysis shows that the alkali activation of Estonian oil shale solid wastes is controlled by the presence and dissolution of reactive Ca-bearing phases. However, the geopolymeric potential of oil shale ashes is limited by the amount of available reactive Si and Al in the source material. Excess Ca in activated samples is precipitated as Ca-hydroxide showing Si deficiency in the system. To induce a substantial polymer formation, additional sources of readily available Si and Al must be introduced in the mix design. In addition, for industrial applications, further optimization of the mix design and curing conditions, including thermal curing, is needed to reduce dry shrinkage and microstructural cracking.*

Keywords: *alkali activation, geopolymer, oil shale ash, solid heat carrier retorting ash.*

1. Introduction

Alkali activated materials represent a novel and environment friendly binder system where cementitious binder is formed through alkali activation of silicate precursors. These materials can be of very different composition and origin, and among them are geopolymers that can be considered as a subset of alkali activated materials with a three-dimensional aluminosilicate binder phase structure [1]. Formation of geopolymers occurs when the aluminosilicate raw material is dissolved in an alkaline solution, and aluminate and silicate species are released into an aqueous phase, forming a complex colloidal solution of silicate, aluminate and aluminosilicate species. Geopolymers can provide the mortar and concrete with mechanical performance

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similar to that of ordinary Portland cement system, with high fire and acid resistance, and can be used to stabilize/solidify different wastes including heavy metals [2]. It is also pivotal that the production of geopolymeric binders is, compared with ordinary Portland cement, ca 60% more energy efficient and the associated carbon dioxide emissions can be up to 80% lower [3]. Geopolymeric binders can be produced from any naturally occurring or industrially produced aluminosilicate raw materials [1]. The secondary usage of different industrial by-products and solid wastes as precursors of geopolymeric binders is specifically beneficial and can significantly reduce the amount of industrial waste otherwise landfilled.

Raw materials and their processing conditions determine the structure and chemical and physical properties of formed geopolymeric products. On a macroscopic scale, geopolymers synthesised from different aluminosilicate sources may appear similar but their microstructure homogeneity and thus the physical, mechanical and also chemical properties vary to a large extent [4]. In addition to different types of slags and the waste from the glass manufacturing industry, combustion of fly ash, a widespread industrial waste, can also be potentially useful for production of geopolymeric alkali activated materials. Commonly, class F-type low-Ca fly ash is used for geopolymeric binder production [5]. However, also class C ashes, i.e. high-Ca fly ashes, have been successfully tested for geopolymeric binder production [6–8]. Valorisation of different solid industrial wastes through alkali activation is recognized as one of the most viable options for the reuse of these types of wastes [9, 10].

In Estonia, more than 70% of the energy sector relies on the mining and processing of Ordovician marine kerogenous oil shale [11]. Estonian oil shale industry is the largest oil shale processing operation in the world today and at current production rates ca 19 Mt of oil shale is mined annually and mostly used at thermal power plants for electricity and heat production (ca 80% of the mined shale) whereas ca 19% of the mined oil shale is used for retorting shale oil and shale gas [12]. Oil shale is a Ca-rich solid fuel of low calorific value and ca 40–50 wt% of the processed shale remains as a solid waste, the majority of which, about 98%, is landfilled.

In earlier years, oil shale ash was to some extent used as a constituent in Portland cement, in road construction, for agricultural purposes [13, 14], and as a filter material in waste water treatment [15–19]. Nevertheless, the secondary reuse of ash is only a token (about 2%) of its annual output and most of it (about 98%) is deposited in large ash fields (plateaus) next to power plants. If the finest fractions of the fly ash from thermal power plants with a lime (CaO_{free}) content less than 10% are still used as an additive to Portland cement, then solid residues from shale oil retorting are currently not used in any beneficial purpose and are landfilled [20, 21]. It is therefore important to find sustainable applications for oil shale solid residues, and synthesising geopolymeric materials that are potentially useable in the building and construction industry could be one of the viable options. Reuse

of this waste would also help to reduce the overall CO₂ footprint and energy consumption of the oil shale industry that is responsible for producing more than 70% of the CO₂ emissions in Estonia [22].

The geopolymeric potential of Estonian oil shale industry residues has been addressed in several case studies in recent years [23–26]. The goal of this contribution is a comprehensive analysis of available data published on alkali activation of Estonian oil shale processing wastes and is mainly aimed at analysis and synthesis of the geopolymerization potential of different Ca-rich Estonian oil shale processing residues, including the oil shale ash produced in Estonian thermal power plants (TPP), and shale oil processing ash remaining in solid heat carrier (SHC) retorts.

We focus on the characterization of the effects of different alkaline activator solutions on the polymerization of Estonian oil shale processing residues, the structural, chemical and mineralogical properties of possible depolymerization-repolymerization reactions and the respective products in alkali activated materials, as well as the characterization of cementitious properties of the alkali activated residues.

2. Properties of the oil shale processing residues

Oil shales are sedimentary rocks that contain bituminous organic matter which can be pyrolyzed to extract shale oil and combustible gas or burnt 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 a few countries, including Brazil, China, Israel, Estonia and recently Jordan [27], mainly because of its low calorific value. However, the use of oil shale as a primary source for energy is foreseen to increase worldwide in the coming decades.

Depending on oil shale processing technology there are two major types of solid residues: residues from thermal power plants and those from shale oil retorting plants.

2.1. Thermal power plant residues

Oil shale is burned in thermal power plants for electricity and heat generation using pulverized firing (PF) or circulating fluidized bed (CFB) combustion technology with temperatures reaching about 1450 °C and 700–850 °C, respectively [12]. The resultant oil shale ash is a light-coloured mineral material that is composed of lime, calcite, anhydrite, different secondary Ca-silicate phases and residual non-carbonate fraction in varying proportions. The composition of the waste depends on processing technology and oil shale feed composition. The remaining ash is Ca-rich with a CaO content as high as 55 wt% [20]. Compared to ash wastes from other sources, oil shale ash is, by its composition, most similar to type C fly ash from coal combustion. The structural, chemical, mineralogical and physical properties of oil

shale ash have been thoroughly studied and presented in the last decades [20–29].

2.2. Shale oil retorting residues

Oil shale processing into shale oil and shale gas is performed using either Kiviter or solid heat carrier process (e.g. Galoter, Petroter or Enefit process) [21, 30]. In Kiviter process, hot gas is used as a heat carrier, whereas in SHC process hot spent shale formed in the same retorting process is used as a heat carrier. Currently, there are two major SHC technology modifications used for shale oil production in Estonia – Petroter technology is used at Viru Keemia Grupp and Enefit at Eesti Energia. During retorting oil shale is heated in the absence of oxygen to a temperature at which its organic part – kerogen – is decomposed or pyrolysed into gas, condensable oil and solid residue, while the inorganic mineral matrix is retained in the form of spent shale.

Shale oil retorting produces two types of waste depending on the technology used – blackish semi-coke from Kiviter process and dark grey retorting ash (also known as black ash) from Galoter, Petroter and Enefit140 SHC processes. A recent modified version of SHC process applied in the Enefit280 technology leaves a light-coloured ash residue similar to that produced in CFB boilers [31]. Semi-coke from Kiviter process is a heterogeneous granular material that is rich in organic residues (up to 10 wt%), including phenols, polycyclic aromatic hydrocarbons (PAHs) and oil products that are potential pollutants with harmful environmental effect [21]. Although additional recycled gas and air are admitted to the chambers at the final stage of retorting to burn off the organics from the residue [32], the burnout is typically inefficient but due to short residence time. Because of high organic material content the semi-coke does not show potential for geopolymerization and has not been tested in any of the earlier studies.

Black ash from Petroter SHC process is however more similar to combustion ash, and contains only a few percent of organics [33, 34]. The physical, chemical and mineralogical properties of black SHC retorting ash have been studied by Talviste et al. [34].

Recently, Eesti Energia AS, the largest Estonian oil shale mining and processing company, introduced a new Enefit280 technology that, by its nature, is an enhanced Enefit140 SHC retorting system, based on Galoter process. The Enefit280 retorting unit is combined with the CFB combustion boiler where the spent shale and flue gases are combusted at 800 °C to produce electricity. As a result, the Enefit280 technology is more energy efficient and its overall impact on the environment is reduced, compared to other retorting systems currently in use [31].

The composition of the Enefit280 ash is significantly different from that of the other retorting residues produced either in Kiviter type retorts (semi-coke) or other Galoter type SHC retorts, including Petroter and Enefit140 (black ash). The ash is grey-beige and does not contain any significant

amount of residual organic carbon. This ash does not contain CaS (oldhamite) and partly oxidised Fe-oxide mineral magnetite [Fe_3O_4 ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$)] that are characteristic of ashes from older SHC retorts [21, 34] where the waste forms under oxygen deficient conditions. In this sense this ash can be considered to be similar to TPP ashes, particularly to those formed in CFB boilers. However, the content of several reactive phases (e.g. belite-C2S), which are responsible for hydraulic self-cementing, are low in the Enefit280 waste heat boiler (WHB) ash [24] when compared to other SHC or any other TPP ashes [28, 29, 34, 35].

3. Geopolymeric potential of Estonian oil shale processing residues

Reactive components potentially used for geopolymers represent a wide range of different materials. Typically clay and/or natural pozzolanic materials [1] like volcanic ash are considered as primary materials for geopolymeric binders. Also, a variety of secondary materials like slags and ashes from different processes can be used. All of these have considerably diverse starting compositions and result in a large variety of alkali activation reaction products. The “classical” geopolymers are based on aluminosilicate raw materials such as kaolin clay and/or aluminosilicate fly ashes that form strong aluminosilicate polymer networks upon alkali activation [1]. On the other hand, slags with high CaO content develop cementitious calcium-silicate-hydrate (C-S-H) and calcium-aluminium-hydrate (C-A-H) phases that are formed in ordinary Portland cement hydration [8]. Therefore, to achieve and maintain the good strength and chemical resistance/durability of geopolymeric materials the initial composition and selection of additives and proper activation methods are important.

The availability of reactive calcium plays an important role in the cementation of TPP and SHC ashes in mixtures with plain water [35, 36], which is mainly propagated by the formation of secondary Ca-Al-sulfate phases (ettringite) and Ca-carbonate that precipitates upon CaO_{free} (lime) hydration into $\text{Ca}(\text{OH})_2$ (portlandite) and its subsequent carbonation [34]. In both ash types studied by Paaver et al. [23, 24] and Paiste et al. [25, 26] and activated with NaOH and Na-silicate, ettringite was found to be absent and Ca-carbonate formation was subdued. Spectroscopic analyses using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FT-IR) and solid state ^{29}Si magnetic angle spin nuclear magnetic resonance (^{29}Si MAS-NMR) analysis of these ashes activated with NaOH, Na-silicate and Na-silicate/NaOH show that polymerization processes occur [25, 26]. However, ^{29}Si MAS-NMR data suggest that the polymerized silicate structures formed in the alkali activation of fresh TPP ashes are one-dimensional and do not contain chain branching and cross-linking tetrahedra that are formed in activated SHC ashes, with the latter feature being

characteristic of a three-dimensional geopolymer structure. Additionally, analytical scanning electron microscopy (SEM) spectra indicate that the amorphous matrix formed in activated SHC ash contains a notably higher amount of Al (7 wt%) compared to the phase formed in activated TTP ashes (1 wt%), indicating a higher degree of Al substitution [23, 24, 26].

Nevertheless, it should be considered that the high Ca content in oil shale ashes is not common for a typical geopolymer structure, which is a hydrous alkali aluminosilicate with a tetrahedral silicate network and a number of tetrahedral positions occupied by Al^{3+} in four-fold coordination, charge stabilised by an alkali cation [1]. Also, there can be some Al-O-Al groups and non-bridging oxygen of the form Si-OH, $\text{Si-O}^- \text{Na}^+$ or Al-OH existing in the system [37, 38]. On the other hand, Yip et al. [39] have proposed that in the presence of elevated calcium concentrations in the geopolymeric system, a C-S-H based cementitious material may form instead. Indeed, as mentioned above, the ^{29}Si MAS-NMR analyses of studied TPP and SHC ash mixtures show that a C-(A)-S-H phase with a chemical shift typical of a system saturated with Na^+ has formed, which is further supported by the behaviour of Si-O(-Si/Al) stretching bands in ATR-FT-IR spectra of activated materials [25, 26].

Several earlier studies have shown that the CaO in the source material used for geopolymerization appears to strengthen the geopolymer by the decrease of microstructural porosity and formation of amorphous Ca-Al-Si gel [39–41]. The elevated calcium content in the solid raw material affects the process of geopolymerization by providing extra nucleation sites for precipitation of dissolved species [42]. Formation of (Na)-Ca-Al-Si gel was evident from the analytical SEM spectra of amorphous masses in Na-silicate and Na-silicate/NaOH activated samples made as reported by Paaver et al. [23, 24, 26] with both TPP and SHC ashes.

Our studies, however, show that excessive calcium and high pH (activity of hydroxide ions) in the initial synthesising solution causes precipitation of $\text{Ca}(\text{OH})_2$ (portlandite), which later reacts with CO_2 in the atmosphere forming calcite, resulting in the deterioration of the polymeric product. This feature is evident in all experimental mixtures based on 5M NaOH [26]. Portlandite also appears in mixtures of TTP ashes prepared with Na-silicate containing activators, but is absent in SHC based samples. This difference in excess calcium between TPP and SHC results from the amount of reactive Ca-bearing phases in the respective materials.

The initial compressive strengths achieved with sodium silicate based mixtures agree well with the formation of polymeric structures apparent from ^{29}Si MAS-NMR and ATR-FT-IR data reported by Paiste et al. [25, 26]. However, though the polycondensation in Na-silicate and Na-silicate/NaOH activated mixtures was found to progress with aging and the polymerized chains were growing in length, the measured compressive strength values were lower in aged samples (7 days of curing vs 28 to 90 days of curing). This was evidently due to strong dry shrinkage and formation of abundant

microcracks observed in the polymerized samples, particularly in the SHC ash [23, 24]. Although longer curing times lead to the formation of a structurally longer and more polymerized aluminosilicate binder phase and this trend can be expected to continue with time, the coherence of the sample is lost [23, 24, 26]. As a result, though the binder phase itself is at molecular level getting stronger, it does not contribute to the increase in mechanical strength of the samples. Dry shrinkage is not observed in samples activated with NaOH, however, this material was found to show very low initial compressive strength values though the further increase of the strength correlates well with the dissolution and development of the silicate structures in NaOH activated samples. Shrinkage and creep are typical processes observed in systems based on cement and geopolymer binders [43], which results mainly from drying shrinkage that can be controlled by selecting optimum curing temperature and liquid-to-ash ratio.

Overall, these experimental studies [23–26] suggest that Estonian oil shale ashes do not show very good geopolymerization properties, which is evidently related to the characteristics and content of potentially reactive phases/components. In general, the composition of Estonian oil shale ash produced either in thermal power plants or in shale oil retorting processes is considerably different from that of the raw materials typically used for producing geopolymeric binders [23–26]. By its composition oil shale ash could be considered a class C fly ash that is a Ca-rich ash (CaO content > 20 wt%) and can be and is used to produce geopolymers with considerable final strength [6, 8]. Indeed, the variation of the chemical composition of oil shale ashes of different origin [12–14, 31–35, 42] agrees (or is somewhat higher) with the relative CaO content reported in several other geopolymer raw materials (Fig. 1).

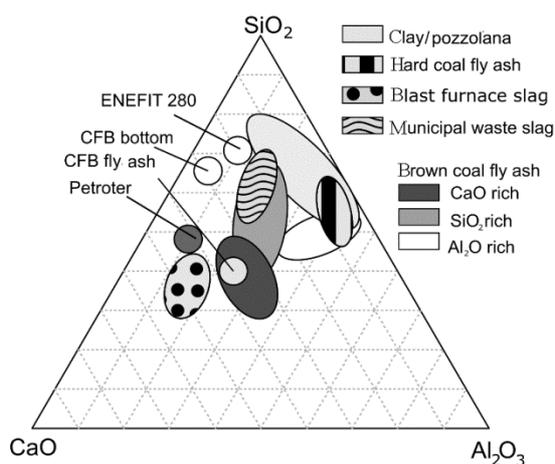


Fig. 1. Classification of potential raw materials used for geopolymers on CaO-SiO₂-Al₂O₃ ternary plot. Modified after [45]. Data for Petroter ash are from [23], for Enefit ash from [24] and for oil shale CFB ashes from [20].

At the same time, the specificity of Estonian oil shale ashes is, compared with other raw materials, the consistently lower proportion of Al_2O_3 (typically < 10 wt%). Duxson and Provis [44] developed a classification system for geopolymer aluminosilicate source materials based on the molar contents of silica, alumina, and combined network modifiers based on charge-balancing capacity whereas the network modifier content was used to quantify the relative amount of alkali and alkali earth metals (Ca^{2+} , Mg^{2+} , Na^+ , K^+) present in fly ash. Estonian oil shale ashes fall off the compositional fields of other raw materials, including (meta)kaolin clay, and F- and C-type fly ashes (Fig. 2), mainly because of the lower Al content. This compositional characteristic by itself dictates that the formation of strong aluminosilicate polymer networks does not contribute to or is subdued in the development of uniaxial strength. The high content of alkali elements (network modifiers), as in oil shale residues, would potentially provide charge balancing by balancing the negative charge of tetrahedral aluminium [44]. This makes aluminium stay in 4-coordination, which has a higher solubility than the 6-coordination form and, as a result, more Al would be available for geopolymerization and fly ashes with higher network modifying agents generally produce stronger geopolymers.

The network modifier content in all types of oil shale ashes is higher or in the same range as in the raw materials producing the strongest geopolymers. However, there is evidently a substantial deficiency of Al, suggesting that in oil shale ashes the development of strength is limited not by the availability of network modifiers, but by the low content of potentially soluble silica and specifically aluminium phases. Overall, this means that for production of geopolymeric materials from oil shale processing wastes, the mix design must include a source of available Si and Al in combination with an

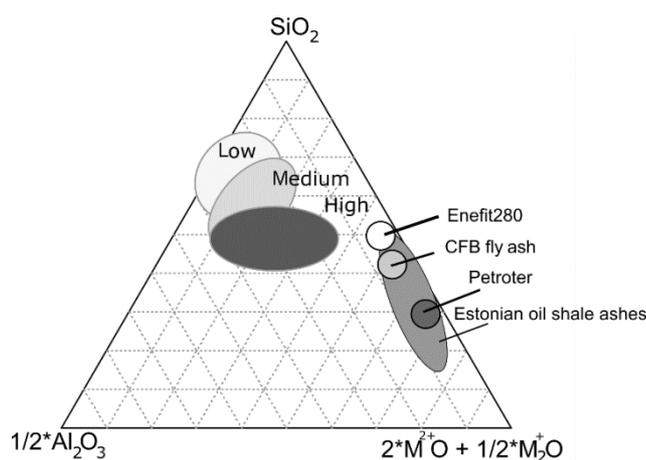


Fig. 2. Ternary plot showing the relationship between geopolymer compressive strength and fly ash oxide composition. Modified after [46]. Data for Petroter ash are from [23], for Enefit ash from [24] and for oil shale CFB ashes from [20].

appropriate activator mixed at an optimum ratio to induce a sufficient degree of depolymerization-repolymerization reactions.

4. Conclusions

Experience from the alkali activation of Estonian oil shale solid wastes shows that polymerization reactions are controlled by the presence and dissolution of reactive Ca-bearing phases. The geopolymeric potential of oil shale ashes is limited by the amount of available Si and Al in the source material. Excess Ca in activated samples is precipitated as portlandite [Ca(OH)_2] and its formation shows Si deficiency in the system, with respect to polymer formation. To induce a substantial polymer formation, additional sources of readily available Si and Al must be introduced in the mix design.

Activation of oil shale solid ash wastes with sodium silicate based activator solutions induces the formation of a polymeric C-(A)-S-H type binder phase that forms an amorphous matrix in the material pore space, filling the area between unreacted ash particles. However, the development of dense microfracturing and strong dry shrinkage causes a significant weakening of the material.

For industrial applications, further optimisation of the mix design and curing conditions must be undertaken, with emphasis on reduction of dry shrinkage, including microstructural cracking and increase of available Si and Al sources that could possibly be provided through the addition of another industrial waste product.

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