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**Strength performance of mechanically activated Ca-rich CFBC fly ash  
pastes with added silica**

MSc. Thesis in Geology

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## **Strength performance of mechanically activated Ca-rich CFBC fly ash pastes with added silica**

As the old PC boilers are being replaced by CFBC boilers, more of CFBC ash waste is produced in the Estonian energy sector. Due to the lower cementitious and different chemical properties of the CFBC ash, new methods of recycling should be considered as depositing the ash in landfill poses different problems. Using CFBC ash mixtures as alternative cement binders might be one of the solutions. Motivation for this study came from a previous article where mechanically activated CFBC fly ash showed great compressive strength results. To further enhance the compressive strength, milled glass or glass wool were added in different amounts to test how various concentrations of Si, Al and Ca changed it. Additionally, two smaller tests with cement hardening accelerator and NaOH alkali activator were performed.

T150 – Material technology, P420 – Petrology, mineralogy, geochemistry

*CFBC, fly ash, glass, glass wool, alternative cement*

## **Silikaatse ränilisandi mõju mehhaaniliselt aktiveeritud kaltsiumirikka CFBC lendtuha hüdratiseerumisele ja survetugevusele**

Vanade tolm põletuskatelde asendamine tsirkuleeriva keevkihttehnoloogiaga toob Eesti energiasektorile kaasa suuremad tsirkuleeriva keevkihttuha jäätmed. Probleemide tõttu, mis kaasnevad tsirkuleeriva keevkihttehnoloogia tuhajäätmekuhjetega, seoses madalamate tsementeeruvate ning putsolaansete omadustega tuhas, tekib vajadus uute meetodite järele tuha taaskasutamiseks. Üheks lahenduseks võiks pidada tsirkuleeriva keevkihttuha kasutamist alternatiivse tsemendina. Käesoleva töö idee tuli varasemast artiklist, kus mehhaaniliselt aktiveeritud ehk jahvatatud tsirkuleeriva keevkihttuha survetugevus andis märkimisväärseid tulemusi. Suurendamaks survetugevust veelgi, lisati erinevas koguses klaasi ja klaasvilla, et testida kuidas erinev räni, alumiiniumi ja kaltsiumi sisaldus muudab seda. Lisaks testiti kahte katsesegu nii tsemendikiirendi kui naatriumhüdroksiidiga.

T150 – Materjalitehnoloogia, P420 – Petroloogia, mineraloogia, geokeemia

*CFBC, lendtuhk, klaas, klassvill, alternatiivne tsement*

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## 1. Introduction

The Estonian oil shale, its geology, firing technology, production of oil and waste management, and the industrial impacts on the environment has been studied for more than 100 years. Economic reserves of the Estonian calcareous kerogenous oil shale (OS) kukersite are in the Upper-Ordovician Kukruse Regional Stage. Kukersite oil shale is composed of 10-65% organic and 15-70% of mineral (mainly carbonate) matter. Its calorific value is usually around 7-11MJ/kg. At the moment 80% of OS is burned for heat and electricity in thermal power plants and lesser amounts account for oil and cement production of 19% and 1%, respectively (Ots, 2006). The highest point in OS mining was in the 1980s, where 30 Mt of OS was mined annually and today the average amount mined is around 15-18 Mt. (Ministry of the Environment, 2019)

Two main types of OS firing technologies used in Estonian power plants are pulverized combustion (PC) and circulating fluidized-bed combustion (CFBC). PC technology has high SO<sub>2</sub> emissions of ~2400 mg/Nm<sup>3</sup>, low energy efficiency of ~30% and expensive maintenance costs. To reduce the SO<sub>2</sub> emissions, most of the old PC energy blocks have been upgraded with Novel Integrated Desulfurization (NID) systems, also called DeSO<sub>x</sub>, where SO<sub>2</sub> emissions are scrubbed with CaO but that lowers the efficiency of the energy blocks (Ministry of the Environment, 2019). The rest of the old PC energy blocks without deSO<sub>x</sub> devices that were active until 2019 were being fueled by OS with lower calorific value by while pulverizing, adding limestone to OS, to reduce the SO<sub>2</sub> emissions, but this technique led to higher CO<sub>2</sub> emissions and less energy efficiency. (Ministry of the Environment, 2015)

CFBC technology offers lower atmospheric emissions, more economical OS usage and thermal efficiency (Paist, 2004) as cost-savings of fuel is over 20% and levels of pollution are reduced even more than EU environmental regulations require (Kohv, Heintalu, Mandel, & Link, 2020). The CFBC boilers operate at temperatures of 850 °C and reach over 40% of efficiency, whereas old PC boilers operate at higher temperatures of around 1450 °C and yield less than 30% efficiency (Ministry of the Environment, 2019). The difference in firing temperatures brings forth different mineral composition and structure in the OS ash. With lower firing temperatures, calcite does not decompose and reactions with silicates are inhibited and the content of highly reactive Ca-Si phases and free lime are lower and

therefore CFBC ash cementitious properties are weaker (Gazdič, Fridrichová, Kulísek, & Vehovská, 2017). This leads to problems with depositing the ash in the landfills, as the landfill has less structural strength, but also limits the reuse of the ash materials (Leben, et al., 2019).

The Estonian energy sector has already closed down old PC boilers and the newer CFBC technology has remained, therefore CFBC ash waste (of which 30-40% is bottom ash and 60-70% fly ash) forms the most part of the ash remaining at the power plants. Also, the focus will be more on shale-oil production than heat and electricity production in the coming decades. (Ministry of the Environment, 2015)

Due to OS low calorific value, about 8 million tons of waste is generated every year (Loo, et al., 2018), of which currently only 2% is recycled, resulting in Estonia being one of the largest waste producers per capita in the world (Ministry of the Environment, 2015). OS PC fly ash has been used as a cement binder in the Estonian cement production (Ministry of the Environment, 2019) and CFBC and DeSO<sub>x</sub> ash has been tested for the production of CEM II type of concrete, which has at least 42.5 MPa of compressive strength after 28 days of curing at 20 °C (Hain, et al., 2016; Gołaszewski, Ponikiewski, & Cygan, 2017). DeSO<sub>x</sub> ash mixtures yielded to much lower compressive strength than CFBC and PC ash and the content of chlorides along with CaCO<sub>3</sub> increased as well did demand for more water (Hain, et al., 2016). About 30% of CFBC fly ash mixed with 70% of CEM I type cement showed great results yielding to compressive strength values over 42.5 MPa, the strength class for CEM II types of cements, with environmentally friendly properties (Environmental Investment Centre, 2014). OS ash has been studied and used in road construction (Paat, 2002) and as a liming agent on acidic fields (Pets, et al., 1985).

With CFBC fly ash, higher content of sulfur leads to longer curing time, which limits the fly ash usage in cement. Prevailing issues limiting recycling come from the smaller field of applications, the decreasing need for concrete in the local market and from the non-existing national law standards for the oil shale applications in e.g. road construction and one possibility of refilling underground mines with OS ash, but no practical solutions have been employed (Ministry of the Environment, 2019). Therefore, new further methods of recycling

should be considered to lower the impact on the environment and to give motivation and new investment ideas to the energy sector to recycle more of its by-products.

Paaver, et al. (2020) showed that mechanically activated ash mixtures with water/ash ratio of 0.35 yielded to strength values similar to ordinary concrete and the usage of mechanically activated CFBC ash as a substitute CSA type binder is applicable. However, introduction of soluble silicon and aluminium to high calcium ash could increase the amount of binder phases and could potentially improve cementing properties even further. This research focuses on enhancing the compressive strength of mechanically activated ash with increasing soluble Si and Al content by adding milled glass or glass wool to the ash mixture. As these types of experiments with fly ash are mostly guided by trial and error method due to high variation of fuels used and therefore different phase content and cementing properties occur. A side experiment of the thesis was made by adding cement hardening accelerator and 1M NaOH, to further study the potential alkaline effect on Ca-rich ash cementitious properties.

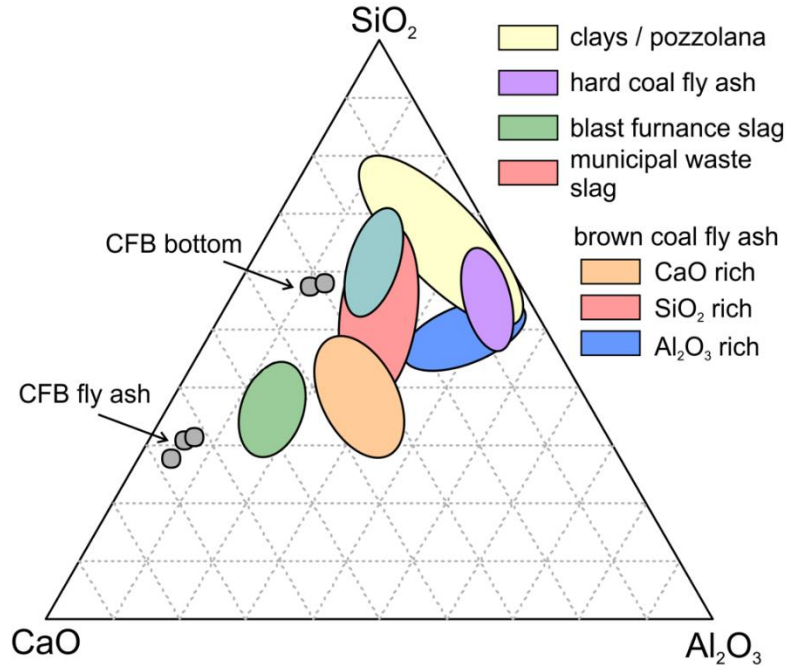
## 2. CFBC ash

### 2.1. Technology

In CFBC boilers the pulverized OS (particles of  $\sim 0.01\text{mm}$ ) is fed to the furnace, where it is circulating at ca  $800\text{-}900\text{ }^\circ\text{C}$  from where ash particles are separated into bottom, circulating (which separates into bottom or fly ash) and fly ash (Figure 1). 30% of CFBC OS ash is bottom ash which is directed from the bottom of the furnace to ash coolers which are drained for ash transportation into landfills. 70% of CFBC ash comes in the form of fly ash which is separated at a multi-level system. The first separation begins in the two-cyclone system, where fly ash with flue gas is directed into the cyclones, where larger particles fall down the inner walls of the cyclone due to inertia. Circulating ash will be redirected into the furnace, bottom ash will be directed to the ash cooler and fly ash with flue gas is transported to the next phase. The two-cyclone system removes ca 10-15% of total ash waste. The next phase is where around 9% of the total ash is separated by the inertia of the particles in the convective pass of the superheater and economizer cyclone and the air preheater cylinder. The most efficient of the separation systems is the electrostatic filter, where most (50%) of the total ash waste is caught by the first electrostatic field. The second electrostatic field catches around 7% of total ash with lower amounts caught by the rest of the fields. The last phase is the bag filter, where 99% of the fly ash left is caught. The maximum amount of fly ash concentration that emits into the atmosphere must be less than  $10\text{mg}/\text{Nm}^3$ . The amount of fly ash is ca  $0.2\text{ mg}/\text{Nm}^3$  after it has gone through the last separation phase, which is the lowest value ever in the OS industry. (Pihu, et al., 2017; Ministry of the Environment, 2019)







**Figure 2.** CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary plot for the classification of different Estonian energy sector waste. Modified after Buchwald et al. (2005); Bityukova, et al., (2010) and Paaver (2016).

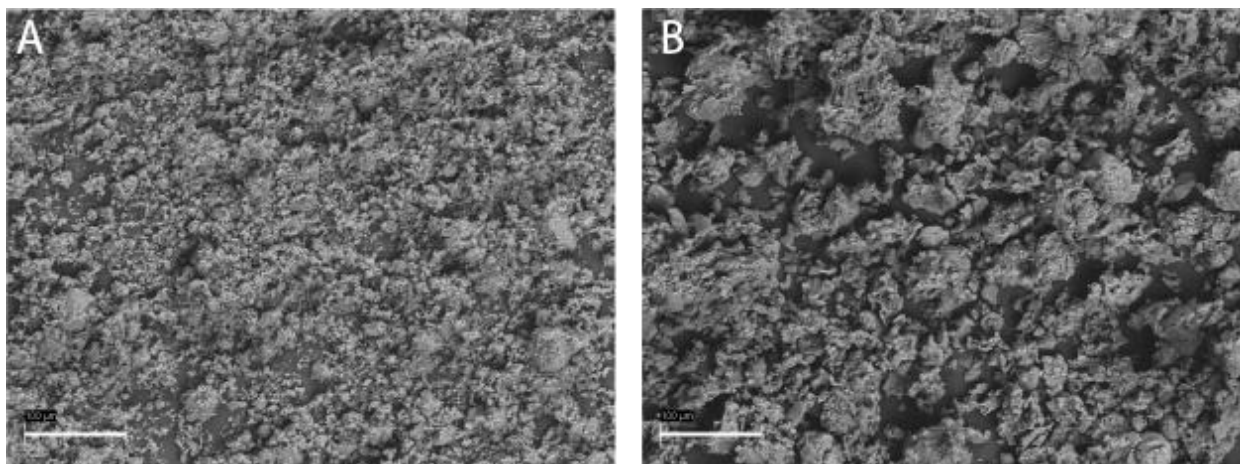
The chemical composition of the CFBC is mainly Ca (26-50%), Si (25-34%), Mg (4-5%), Al (2-11%), Fe (~4%), S (~7%, but varies greatly) and Ti (~0.3-0.5%), which also corresponds to its mineral composition. Ca content is mainly represented in the residue phases of calcite, free CaO and secondary calcium silicate. Mg is found in the form of MgO and as secondary calcium magnesium silicates, but the content of Mg varies greatly due to the natural occurrence of dolomite. Silica is mainly represented as quartz and other primary silicates, but a substantial amount comes in the form of reactive secondary calcium (magnesium) silicates and amorphous glass. Usually bottom ash has lower Si content of <20%. With both PC and CFBC technology the Al content as Al<sub>2</sub>O<sub>3</sub> remains around 2-11% but the content rises as the particle size reduces in the last fields of electrostatic filter separation system and Al content is therefore associated with the mineral phase of aluminosilicates and the amorphous phase of glass. Fe is mainly in the form of Fe<sub>2</sub>O<sub>3</sub> (hematite) or in the lesser form of calcium aluminoferrite and the content rises step-by-step in the separation system from 3% in bottom ash to 5% in the electrostatic filters. S varies greatly with the highest content in the INTREX

ashes, as the heat exchange system is developed to separate the  $\text{SO}_2$  from the flue gas. Usually S comes from the ashes of both PC and CFBC boilers in the form of calcium sulfate or from the oil industry as in the form of CaS. Ti is usually represented in the structure of iron oxides or micas and limited amount of around  $<0.2\%$  as  $\text{TiO}_2$ . (Ministry of the Environment, 2019)

### 3. Materials and Methods

The fresh unhydrated fly ash used in this research comes from the Balti Thermal Power Plant CFBC boiler No. 8, that has been in commission since 2004, after replacing the previous PC boiler. In CFBC boilers, about 60% of fly ash is separated by electrostatic filters from the total ash amount (Paaver et al., 2020).

The fly ash was mechanically activated using a laboratory scale planetary ball mill (RETCHE) with 20 mm-size balls in 0.5 kg batches for 3 minutes at 500 rpm. The milling time was chosen due to the efficiency of grinding process. In a ball mill, efficiency decreases with milling times exceeding 6 minutes due to the material sticking to the balls and sides of the containers. After 8 minutes of milling, specific surface of the ash increases less than 5% as with 4 minutes of milling, therefore it is observable that milling efficiency decreases with the increase in milling time (Paaver et al., 2020). Milling breaks up typically large  $>20\ \mu\text{m}$  size porous lumps of the agglomerated ash particles in raw ash (Figure 3).



**Figure 3.** SEM images of milled (a) and raw (b) CFBC ash.

Glass wool and bottle glass was crushed with a laboratory jaw crusher and then milled using a laboratory scale planetary ball mill. Bottle glass was milled for 2 minutes at 500 rpm and glass wool for 1 minute and 30 seconds at 500 rpm. Glass wool was milled for a shorter period of time and in smaller batches than bottle glass due to the milled wool sticking to balls and to sides of the container, decreasing the milling efficiency. Milling for under a minute was not efficient and lumps of wool in the milling container remained unbroken. Over 2

minutes of milling the material started to agglomerate again and there was not a significant impact on the efficiency of the milling, compared to the 1 minute and 30 seconds, therefore the latter was chosen as the optimal time frame.

Raw and milled ash were mixed with water/ash ratio of 0.35. 1 wt%, 5 wt% and 10 wt% of glass or glass wool was added to mixtures. Also, two separate ash paste bodies, milled fly ash with added  $\text{Ca}(\text{NO}_3)_2$  and water and 1M NaOH and water, were measured to see the reaction of the fly ash with soluble Ca as cement hardening accelerator and an alkaline solution enhancing the silica polymerization reactions. With  $<0.35$  water/ash ratio, filling of the mould was ineffective in some cases due to the paste's poor workability and higher water/ash ratio lowers the compressive strength. As with ordinary portlandite cement, the lower water to ash ratio helps the cementing process, however it also decreases workability which may lead to lower compressive strength due to the increased caps and pore spacing in the specimens (Paaver, et al., 2020).

The pastes were poured into 50x50x50 mm moulds in three replicas and placed on a vibrating plate for 1 minute. The samples were then left to cure at room temperature of  $\sim 20^\circ\text{C}$  and humidity of 50-60% for 24 hours. After 24 hours, all samples were submerged in water for 7 and 28 days. Milled ash samples with added milled glass, milled glass wool,  $\text{Ca}(\text{NO}_3)_2$  and NaOH were left to cure for 90 days. After 7, 28 and 90 days, uniaxial compressive strength tests were performed for the raw and milled ash pastes with additives. The method to measure uniaxial compressive strength was continuous loading under the pressure of  $20 \text{ kPa}\cdot\text{s}^{-1}$  until the test samples fractured.

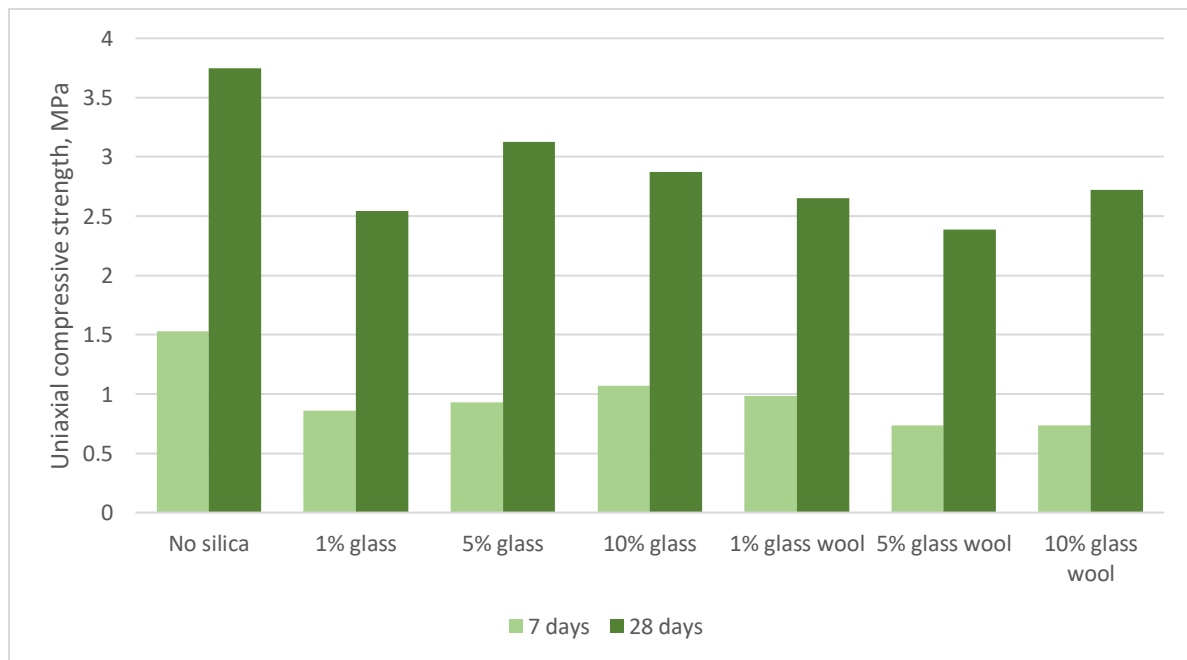
X-ray fluorescence spectrometry on Rigaku Primus II XRF spectrometer using SQX quantification model was used to determine the chemical composition of bottle glass and glass wool. X-ray diffraction (XRD) analysis on a Bruker D8 Advance diffractometer in randomly oriented pressed powder samples using Ni-filtered  $\text{CuK}\alpha$  radiation and LynxEye linear detector over the  $2-70^\circ 2\theta$  region was used for selected samples to determine the mineral composition of the ash pastes. Zeiss EVO15MA SEM with Oxford X-MAX energy dispersive detector was used to determine the microstructure and mineral composition of the 90-day ash bodies.

## 4. Results

### 4.1. Uniaxial compressive strength

Uniaxial compressive strength was measured for raw ash and milled ash pastes with different concentrations of added silica.

Both raw ash and milled ash mixtures were measured after 7 and 28 days of curing but milled ash samples were also measured after 90 days of curing. Compressive strength values of raw ash mixtures yielded only in a slight increase from 0.74 MPa after 7 days to 3.13 MPa after 28 days of curing (Figure 4). Raw ash with added silica had similar results and differed to only a limited extent. Compared to results of Paaver et al. (2020) raw ash pastes with added silica yielded to similar compressive strength results as raw ash pastes with no added silica after 7 and 28 days of curing with similar water/ash ratio, suggesting that added silica did not had any measurable effect on strength development in raw ash pastes, and in fact the added silica gave slightly lower strength values compared with plain raw ash samples.

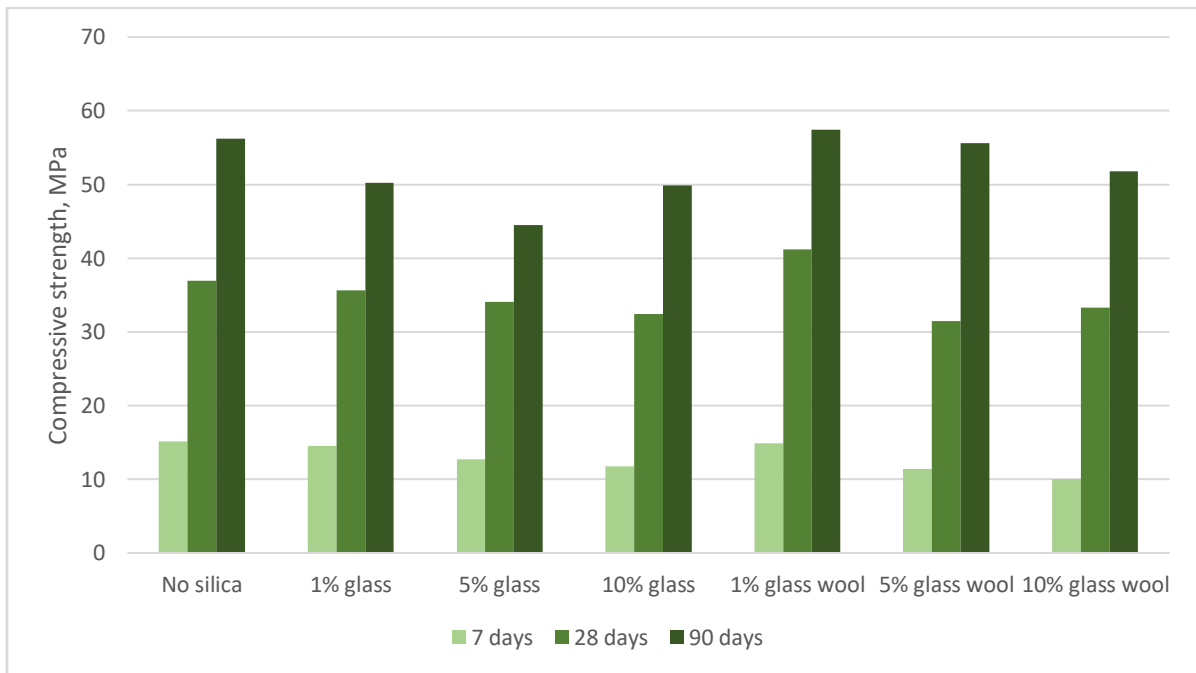


**Figure 4.** Uniaxial compressive strength for raw ash mixtures with different content of silica after 7 and 28 days of curing.

Behaviour of mechanically activated ash in mixtures with added silica was different. After 7 days of curing, milled ash mixtures with 1 wt%, 5 wt% and 10 wt% of bottle glass or glass wool yielded to similar results. For the 1 wt% of silica content for both glass and glass wool, the compressive strength was 14.5 MPa and 14.9 MPa, accordingly (Figure 5).

Approximately a 6 MPa difference was noticed after 28 days of curing between the 1 wt% paste/silica ratio of glass or glass wool ash mixtures. The samples had significantly higher compressive strength, of which the most was for 1 wt% of glass wool with a value of 41.2 MPa. Other samples gave approximately a three-fold of higher values compared to the 7-day results (Figure 5).

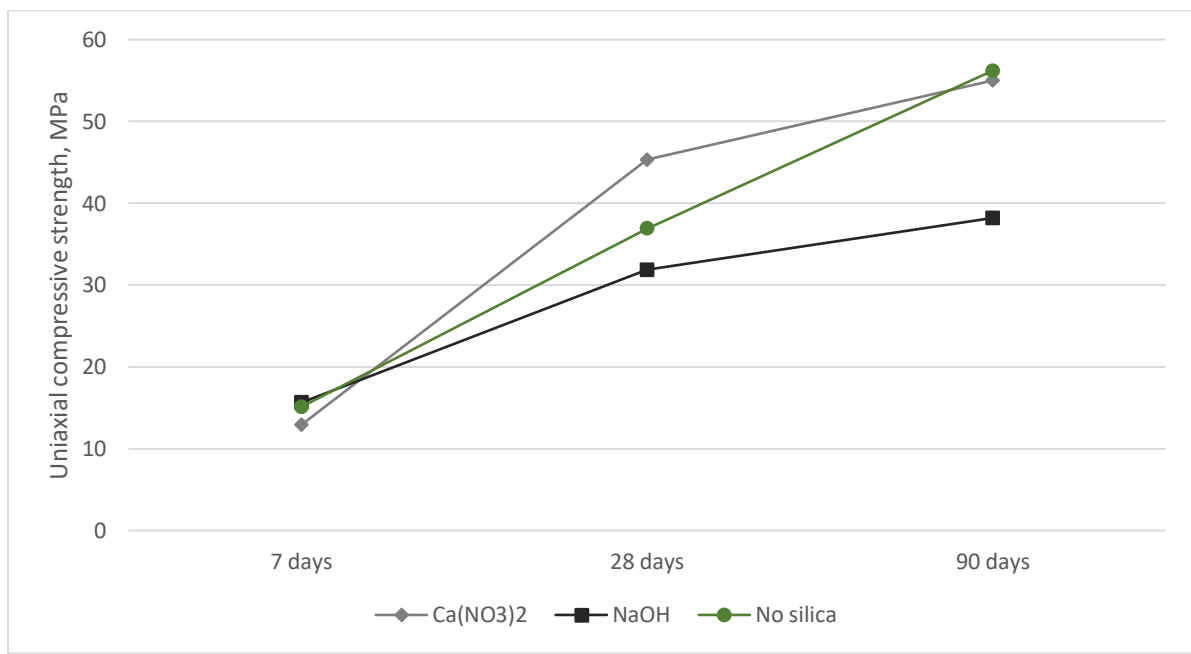
After 90 days of curing the strongest of the samples was the ash mixture with 1 wt% of glass wool yielding 57.4 MPa. All the mixtures with added glass wool reached over 50 MPa, compared with the mixtures with added glass, of which only 1 wt% of the glass in the mixture reached to 50.2 MPa, therefore glass wool seems to be a better reactant than bottle glass (Figure 5).



**Figure 5.** Uniaxial compressive strength for milled ash mixtures with different content of silica and  $\text{Ca}(\text{NO}_3)_2$  and  $\text{NaOH}$ .

In activated ash mixture with cement hardening accelerator the highest result for the  $\text{Ca}(\text{NO}_3)_2$  after 28 days, 45.3 MPa (Figure 6), which is even higher than for the 1 wt% glass wool mixture (Figure 5). After 90 days the cement accelerator mixture continues to show a high value of 55 MPa, similar to the highest values of the mixtures with no silica, 1 wt% and 5 wt% of glass wool.

NaOH mixture showed (Figure 6) relatively good compressive strength rise from 7 to 28 days but after 28 days the compressive strength did not increase at the same rate as in other mixtures.



**Figure 6.** Uniaxial compressive strength for milled ash mixtures with added  $\text{Ca}(\text{NO}_3)_2$  and NaOH.

#### 4.2. Chemical composition of the ash, bottle glass and glass wool

Raw fly ash is mainly composed of  $\text{SiO}_2$  and  $\text{CaO}$ , 35.2 wt% and 29.8 wt %, respectively (Table 1).  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  content in the ash is 8.5 wt%, 4.0 wt% and 5.1 wt%, accordingly. The sulphur content in the form of  $\text{SO}_3$  is 6.7 wt% and is high as for all CFBC ashes. (Paaver, et al., 2020)

**Table 1.** Chemical composition of the raw ash, wt%. L.O.I – loss on ignition at 950 °C (Paaver, et al., 2020)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	L.O.I.
35.19	8.47	0.49	3.98	0.06	29.81	5.07	0.11	4.25	0.15	6.74	4.71

Chemical composition of bottle glass is dominated by 69.6 wt% of SiO<sub>2</sub>, 12.4 wt% of Na<sub>2</sub>O and 9.4 wt% of CaO (Table 2). Glass wool shows lower values of 46.0 wt% SiO<sub>2</sub>, 11.8 wt% Na<sub>2</sub>O and 5.1 wt% CaO. B<sub>2</sub>O<sub>3</sub> content shows a value of 11.7 wt% in glass wool and 4.0 wt% in bottle glass. Al<sub>2</sub>O<sub>3</sub>, MgO and SO<sub>3</sub> values of 1.5 wt%, 1.7 wt% and 1.4 wt% are slightly higher in glass wool compared to bottle glass. Additionally, glass wool composes of 9.1 wt% of C, whereas bottle glass has little to none C content.

**Table 2.** Chemical composition of glass wool and bottle glass, wt%. L.O.I – loss on ignition at 950 °C

Oxide	Glass wool	Bottle glass
SiO <sub>2</sub>	45.94	69.56
Al <sub>2</sub> O <sub>3</sub>	1.54	1.43
TiO <sub>2</sub>	0.02	0.08
Fe <sub>2</sub> O <sub>3</sub>	0.27	0.41
MnO	0.33	0.06
CaO	5.21	9.38
MgO	1.71	1.14
Na <sub>2</sub> O	11.79	12.4
K <sub>2</sub> O	0.5	0.29
P <sub>2</sub> O <sub>5</sub>	0.01	0.01
SO <sub>3</sub>	1.38	0.11
B <sub>2</sub> O <sub>3</sub>	11.73	4.07
Ba	0.01	0.02
C	9.14	0.62
Cl	0.03	0.03
Cr	0.03	0.05
LOI	10.31	0.31

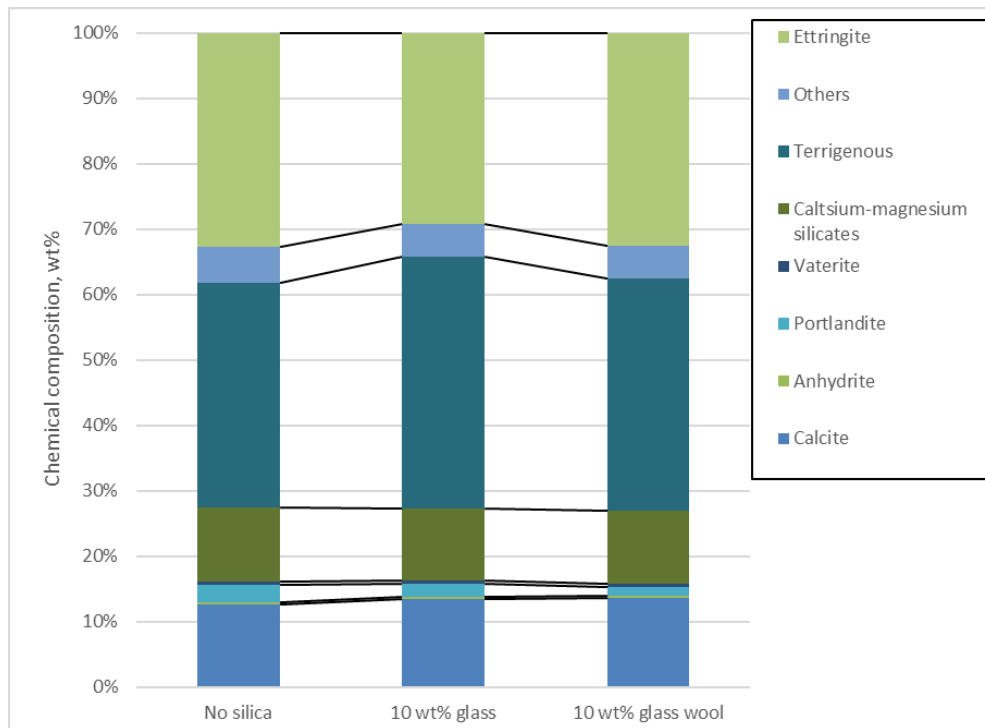


### 4.3. Mineral composition of the ash mixtures

The mineral composition of the 10 %wt glass mixture is dominated by ettringite (29 wt%) and terrigenous minerals (19 wt% quartz, 13 wt% K-feldspar and 7 wt% illite). The content of calcite and calcium magnesium silicates were 14 wt% and 11 wt%, respectively. Compared to the mixture with no silica, ettringite content was lower by 3 wt%. (Figure 7)

Ash mixture with glass wool has similar composition of 33 wt% of ettringite and 36 wt% of terrigenous minerals (17 wt% quartz, 13 wt% K-feldspar and 6 wt% illite). Calcite and calcium magnesium silicate composition was of 14% and 11 wt%, accordingly. Ettringite content remained the same as in the mixture with no added silica. (Figure 7)

For both glass and glass wool mixtures, portlandite content was 1-2 wt% lower than in the mixture with no silica. Merwinite was only noticed in the mixture without added silica, with 0.5 wt%. (Figure 7)



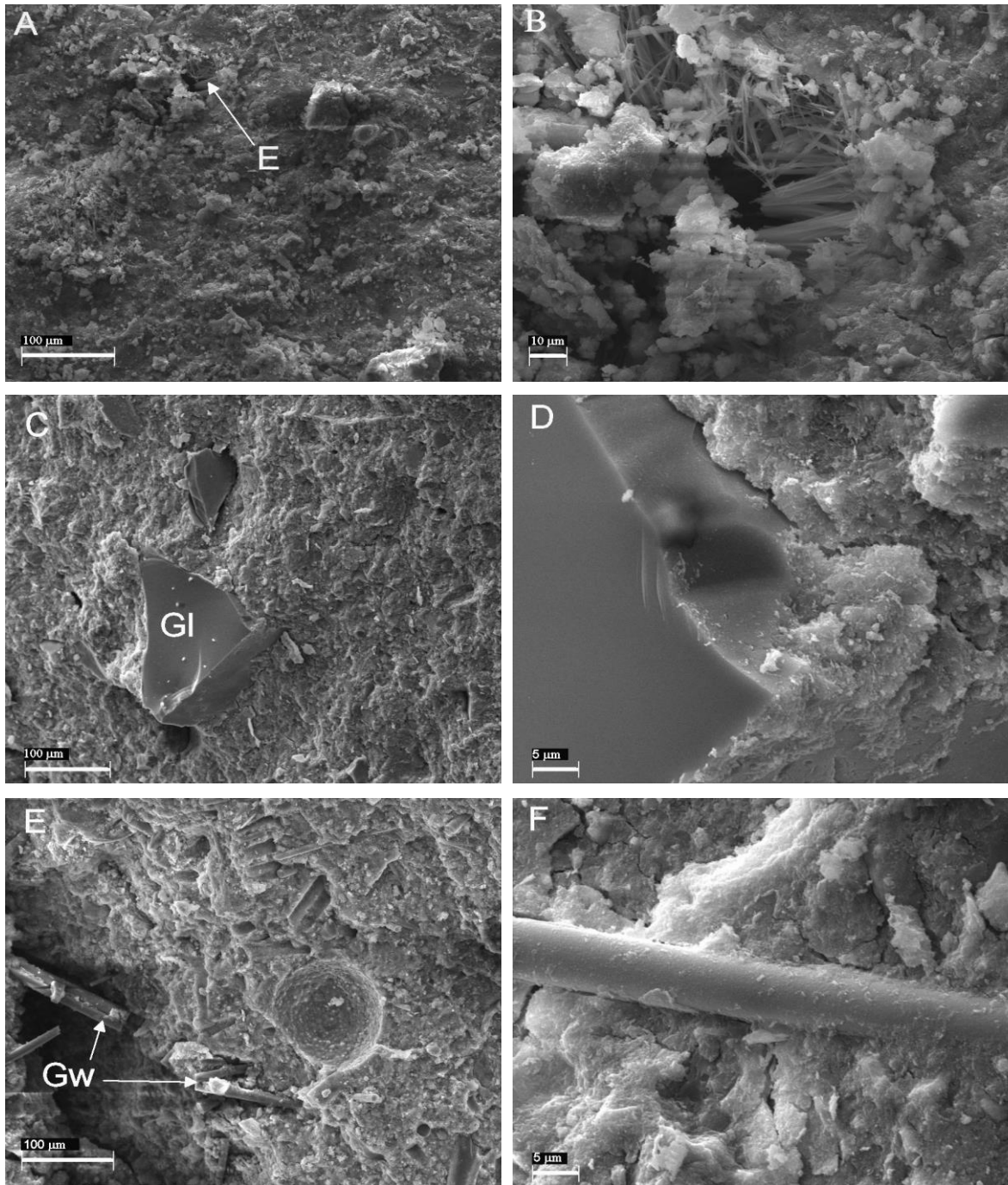
**Figure 7.** Mineral composition of ash mixtures with no added silica, with 10 wt% of added glass and 10 wt% of added glass wool.

#### 4.4. SEM microstructure

The microstructure of milled ash with no added silica shows a compact matrix and the small amount of existing pore space is filled with lath-shaped ettringite crystals (Figure 8a, b). The compact matrix shows very fine grained and C-S-H gel-like masses between the unreacted ash particles.

Mixture with 10 wt% of added bottle glass has similar compact microstructure with ettringite filling the pore space, as ash with no silica, but within the C-S-H gel-like compact matrix, there are glass shards which have a smooth unreacted surface as shown in Figure 8c, d.

10 wt% glass wool ash mixture shows a matrix that is compact and with gel-like to very-fine-grained masses but intertwined with glass wool fibres as seen in Figure 8e. The surface of the glass wool fibre (Figure 8f) shows some precipitates on the surface and dissolution defects which might indicate reaction with the ash matrix and therefore could be associated with the better compressive strength compared to bottle glass mixtures.



**Figure 8.** SEM backscattered images of ash pastes with no added silica (a, b), 10 wt% of added bottle glass (GI) (c, d) and 10 wt% of added glass wool (Gw) (e, f).

## Discussion

As Paaver, et al. (2020) have shown, significant compressive strength increase for the fly ash can be obtained after only 2 minutes of milling in the planetary ball mill, but compressive strength might be also affected by the reactive Al and Si content as shown by Paaver, et al. (2017). In this study Al content in the glass and glass wool (Table 2) is 1.5 wt% for both and Si content is 70 wt% and 46 wt%, accordingly, therefore sufficient amount of Si would be made available, but still the limiting factor to the compressive strength development might come from the low content of Al.

This study shows that bottle glass or glass wool additives did not yield significant compressive strength improvements and adding glass or glass wool to the mixture even lowered the compressive strength compared with no added silica control mixture (Figure 5), except for the slight increase that is noticed after 28 and 90 days of curing with the 1 wt% of added glass wool, that did also show some dissolution/reaction on contacts with the ash matrix. The slight decrease in the strength of the samples mixed with glass could be associated with water to ash ratio, which was calculated for the dry mass of the mixture, whereas glass does not bind with water, and therefore water/ash ratio was higher in these samples, resulting in lower compressive strength. This might also indicate that in the samples mixed with wool, potential strength could be even higher with the corrected amount of water compared to ash samples without additives, since slight reaction was noted on the glass wool fibres in SEM analysis (Figure 8f). It could indicate that lower Si content and very slightly higher Al content compared to bottle glass mixtures might be the reason for the small compressive strength increase compared to the no silica mixture as some C-(A)-S-H-like gel might have been developed. To compare the results of this study, Table 3 shows the compressive strength of most common types of cement.

**Table 3.** Reference values of compressive strength for different types of cement mixtures after curing for 7, 28 and 90 days. Modified after Gazdič et al, (2017).

Cement type	OPC	PCC ash		FBC bed ash		FBC filter ash	
Dosage of ash wt%	0	15	30	15	30	15	30
Grinding time [hour:min]	1:30	2:05	1:55	1:40	0:55	1:00	0:30
Water/binder ratio [-]	0.31	0.3	0.29	0.31	0.33	0.32	0.4
Compressive strength [MPa]							
7 days	59.6	46.2	45.7	57.5	28	48	19.1
28 days	66.5	59.4	59.1	63.9	38.1	59.3	38.3
90 days	69.5	65.8	66.7	76	56.2	63.5	38.9

Samples mixed with  $\text{Ca}(\text{NO}_3)_2$  cement additive showed a slight rise in compressive strength over other mixtures. The effect of this activator is related to the addition of the soluble Ca that allows somewhat quicker setting of the paste and contributes to the development of the early strength.

Adding NaOH solution as alkali activator, the 90-day compressive strength of the ash mixture was significantly lower compared to the other mixtures, although the alkaline NaOH solution is intended to activate the geopolymerization and increase reactivity (Provis & Bernal, 2014). It appears that as strength in activated CFBC ash is provided by formation of ettringite (Paaver, et al., 2020) the alkali activation might actually prohibit the formation of large ettringite networks, therefore resulting in the lower compressive strength.

It should be also considered that 11.7 wt% and 4.0 wt% of boron found in the chemical composition of the glass wool and bottle glass, respectively (Table 2), dissolution of the boron might have an impact on the compressive strength as both mixtures yielded to lower values after 28 days than ash with no added silica. Hubert & Faber (2014), Smith (1986) and Davraz (2015) have shown that boron affects the cement setting time and is used in concrete industry as retarder. Boron is added to glass wool to improve the thermal conductivity and hydrolytic resistance (Marshall & Noble, 2007) and added to glass for lower expansion and melting temperature and higher durability (Smith, 1986).

## Conclusions

As the old PC boilers are being replaced by CFBC boilers, more of CFBC ash waste is produced in the Estonian energy sector. Due to the lower cementitious and different chemical properties of the CFBC ash, new methods of recycling should be considered as depositing the ash in landfills has structural integrity concerns but also limits the reuse of the ash materials. Using CFBC ash mixtures as alternative cement binders might be one of the solutions.

Paaver, et al. (2020) has showed that mechanical activation significantly improves the compressive strength of the CFBC ash. This thesis studied the effect of added silica as milled glass or glass wool to improve the compressive strength of raw and mechanically activated ash.

The uniaxial compressive strength of raw ash pastes with added bottle glass or glass wool yielded low values of only 0.74 to 3.13 MPa after 28 days, therefore compared to the strength of ca 50 MPa for both milled ash with added glass or glass wool after 90-days, the raw ash has minor value in recycling as a cement-type product. Milled ash with added glass or glass wool did not show any significant improvement in uniaxial compressive strength. Milled ash with 1 wt% of added glass wool showed the highest compressive strength which was 1MPa higher than the ash mixture with no added silica, after 90 days, therefore some Si and Al might have reacted in the mixture. Cement hardening accelerator,  $\text{Ca}(\text{NO}_3)_2$ , showed the best results after 28 days of curing and reached to similar values after 90 days as did the 1 wt% glass wool mixture and no added silica mixture. NaOH as alkali activator yielded similar values after 28 days as the other ash mixtures but after 90 days of curing, the compressive strength was significantly lower.

Due to the poor reactivity of glass and glass wool, the soluble Si and Al were not sufficiently released though glass wool mixture with slightly higher compressive strength values show signs of ash matrix and glass wool fiber reactions.

As ettringite is the main mineral that increases the cementitious properties by filling the pores in the cement matrix, less content yielded to lower compressive strength.

The results of this work show that adding glass or glass wool, except for 1 wt% of glass wool which showed a slight increase, did not enhance and even lowered the compressive strength of the milled CFBC fly ash mixtures by significant amount. Cement hardening accelerator showed better results after 28 days of curing than other samples and NaOH as alkali activator did not yield significant results. Overall, mechanically activated ash has definitely high potential for reuse and partial OPC replacement, but at this form the additives do not show a viable gain in strength and need some further research. Future studies should be aimed to study the soluble Al and Si optimal content in the CFBC ash mixture or the use of multiple additives to create a multi-component system to improve the compressive strength.

## **Silikaatse räni lisamise mõju mehhaaniliselt aktiveeritud kaltsiumirikka CFBC lendtuha hüdratiseerumisele ja survetugevusele**

Vanade tolm põletuskatelde asendamine tsirkuleeriva keevkihttehnoloogiaga toob Eesti energiasektorile kaasa suuremad tsirkuleeriva keevkihttuha jäätmed. Probleemide tõttu, mis kaasnevad tsirkuleeriva keevkihttehnoloogia tuhajäätmekuhjetega, seoses madalamate tsementeeruvate ja putsolaansete omadustega tuhas, mis toob kaasa tuhakuuhje struktuuri stabiilsuse probleeme ning lisaks piirab tuha kasutusvõimalusi, tuleks mõelda uutele tuha taaskasutusmeetoditele. Üks võimalikest lahendustest võiks olla tsirkuleeriva keevkihttuha kasutus alternatiivse tsemendi sideainena.

Paaver, et al. (2020) näitas, et tsirkuleeriva keevkihttuha mehhaaniline aktiveerimine tõstab tuha survetugevust märkimisväärselt. Käesolevas töös uuriti, kuidas jahvatatud klaasi või klaasvilla lisamine mõjutab värske või mehhaaniliselt aktiveeritud tuha survetugevust.

Võrreldes klaasi või klaasvilla lisandiga jahvatamata tuha survetugevusi, 0,74 kuni 3,13 MPa peale 28 päeva, jahvatatud tuhaga, millele lisati klaasi või klaasvilla ning mis mõlemad andsid survetugevuseks ligikaudselt 50 MPa peale 90 päeva, on jahvatamata tuhal suhteliselt väike väärtus taaskasutamaks seda tsemendi tüüpi ehitusmaterjalina. Jahvatatud tuha segud lisatud klaasi või klaasvillaga ei andnud paremaid tulemusi ja isegi langetasid survetugevust. Suurim tugevus oli tuhasegul 1 wt% klaasvillaga, mis saavutas kõige suurema survetugevuse ning andis 1MPa võrra parema tulemuse kui ilma klaasilisandita segu, mis võib viidata Si ja Al mõningasele reaktsioonile. Peale 28 päeva tahkumist, andis segu, millele oli lisatud tsemendikiirendi, kõigist kehast kõrgeima survetugevuse ja samuti saavutas antud katsekeha peale 90 päeva kivistumist ligikaudselt võrdväärse tulemuse 1 wt% klaasvilla lisandiga ja ilma klaasi lisandita segudele. Segu, millele lisati NaOH kui leelisaktivaator, andis peale 28 päeva tahkumist sarnase tulemuse kui teised segud kuid peale 90 päeva oli segu survetugevus kõigist madalam.

Klaasi ja klaasvilla halva reageerimisvõime tõttu ei vabanenud piisavalt lahustuvat räni ja alumiiniumi, kuid suurema survetugevusega klaasvilla segu viitab mingil määral tuha maatriksi ja klaasvilla kiudude reaktsiooni.



Ettringiit on põhiline mineraal, mis tõstab tsementeerumisomadusi, täites kivimi maatriksis pooriruumi ning seetõttu madalam sisaldus andis survetugevustes nõrgemaid tulemusi.

Antud töö tulemusel selgus, et klaasi või klaasvilla lisamine tsirkuleeriva keevkihi lendtuha segule ei suurendanud ja isegi vähendas segude survetugevust üsna märkimisväärselt, välja arvatud 1 wt% klaasvilla sisaldusega segu, mille survetugevus näitas veidi kõrgemat tulemust. Tsemendikiirendiga segu näitas peale 28 päeva tahkumist kõige paremaid tulemusi ja segu NaOHga kui leelisaktivaatoriga ei andnud märkimisväärsed tulemusi. Edasised uuringud oleksid vajalikud, sest mehhaaniliselt aktiveeritud tuhk omab suurt potentsiaali taaskasutuse seisukohast ja portlandtsemendi osalise asendajana. Kuna antud kujul lisandite lisamine ei anna märkimisväärselt tulemust survetugevuse tõstmiseks, võiks uurida lahustuva Al ja Si optimaalse sisalduse saavutamist või mitme lisandi kasutamist, et tekitada mitme komponendiline süsteem.

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