

Rockwool waste in fly ash geopolymer composites

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Abstract

Mineral wool waste is often considered unrecyclable, due to its difficult-to-process physical composition, and potential microbial contamination in the post-consumer products. Total mineral wool waste generated in the EU is growing continuously and is currently over 2.3 Mt annually, volumetrically accounting for the largest single waste source in some landfills. Here, we take advantage of the alkali-soluble nature of the rockwool waste, and use a combined mixing and dissolution method to prepare this otherwise unusable waste for geopolymerization, with up to 33% inclusion in the final product. This mixing and dissolution step enables sufficiently high solids content to form a castable geopolymer paste, which forms a rigid matrix and a compressive strength of 12.8 MPa, sufficient for structural applications. This is the first time mineral wool waste has been used as a geopolymer precursor. FESEM and XRD analysis of the formed products were performed to verify geopolymer formation. By using the preparation reported here, otherwise unrecyclable mineral wool waste can potentially be turned into a valuable raw material for geopolymer materials.

1. Introduction

A proper thermal insulation is one of the most effective ways to achieve sustainability and saving energy used for heating and cooling buildings. However, the recyclability of the insulation materials is not often

considered, and is a major bottleneck. Mineral wool—a general term for rockwool and glass wool—is the most common insulation material in buildings worldwide. However, despite energy savings during the use phase, it does not have a favorable overall impact on the environment [1]; mineral wool waste is a major worldwide problem due to the large amounts generated in construction and demolition waste (CDW). It is a waste stream that is often considered unrecyclable. In 2010 the amount of mineral wool waste generated in Europe totaled 2,3 Mt and by 2020 the amount is estimated to be over 2,5 Mt [2]. Due to the low density of mineral wool, it is relatively expensive to transport and requires large landfilling areas.

Because of the importance of reducing the CDW waste, previous studies have considered mineral wool waste to be reused in ceramics [3, 4], cement composites [5–7], fiber-based composites [8], gypsum board, [9–11], and tiles [12]. In some cases, the mineral wool waste can also be recycled back to the manufacturing process by briquetting [13, 14]. However, despite many attempts, the utilization of post-consumer and fine mineral wool waste is still extremely low. Problems in mineral wool recycling cause the fibrous nature of the material in many cases, including cement and gypsum applications, where water demand has to be minimized, and adding a fibrous material drastically reduces the flowability.

To address these challenges, the objective of this work was to develop a method for utilization of mineral wool waste as an inorganic binder, also called geopolymers, with a high fraction of waste materials in the mix design. The term ‘geopolymer’ is used loosely here, with high calcium and magnesium content in the precursor, the exact term would be more cumbersome ‘alkali-activated material’. Geopolymers are alkali-activated aluminosilicate materials, with similarities to ceramics and organic polymers [15]. They are formed at near room temperature by the reaction of solid aluminosilicate material, such as fly ash, with liquid alkali activator. The reaction product in geopolymer processing is a structurally disordered, highly cross-linked aluminosilicate gel and in high-calcium systems a calcium aluminosilicate hydrate [15]. Crystalline zeolite phases can also be present, especially in higher water content gels. [15] Alkali-activated materials have received increasing attention from the scientific community in recent years, due to their promise in drastically lowering CO₂

emissions compared to traditional OPC cement, but also the flexibility that these silicon based inorganic polymers present in terms of material properties and their potential in using secondary raw materials [16–24].

Geopolymers are made by mixing an alkali solution with an alumino-silicate source, that is finely ground and in reactive form. Alumino-silicate source can be waste material, such as fly ash, or fired clays that contain large amounts of aluminum and silicates in soluble form that are dissolved by the alkaline environment created by the activator, most often sodium hydroxide. The ensuing reorientation and solidification of the silicon and aluminum hydrates in polymer-like chains is then responsible for structural strength of geopolymer. In high-calcium systems the main binding phase is an aluminum-substituted calcium silicate hydrate –type gel instead, which has a disordered tobermorite-like structure [15]. Many of the end products are X-ray amorphous, which explains why the structure has only recently been accurately characterized despite it being chemically and thermally highly stable [25].

In terms of chemical composition and mineralogy rock wool offers an ideal precursor for geopolymerization; silicon and aluminum present are soluble, since the fibres are purposefully designed to be in the soluble form due to safety reasons (**Error! Reference source not found.**). Insoluble mineral fibres, such as asbestos, are dangerous when inhaled and therefore man made mineral fibres (MMMF) are designed to dissolve in the normal pH of human body [26, 27]. Despite the high solubility, the physical composition of the fibres poses a bigger challenge when used in geopolymers: they typically compose of 5-10 µm thick fibers, and therefore it is impossible to form a flowable paste by mixing any significant amount of mineral wool in the paste. Fibers increase the need for lubricating water in the paste, which is detrimental to the strength—excess water will escape the matrix when drying, leading to cracking and low compressive strength.

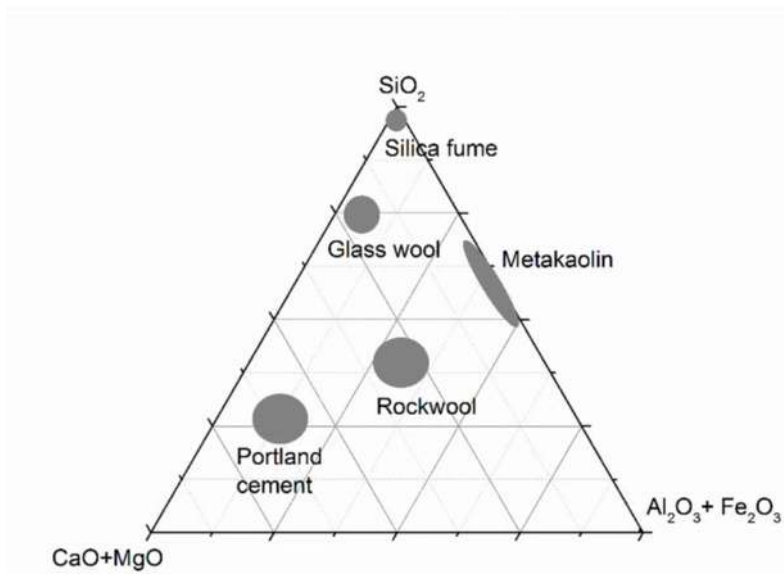


Fig. 1 Chemical compositions of rockwool and glass wool compared to other alkali-activated binders

To answer these difficulties in mineral wool waste utilization, we gradually dissolved the mineral wool fibers in alkali solution by vigorous mixing in high alkali concentration (**Error! Reference source not found.**). This type of preparation enabled sufficiently high solid content of mineral wool in the geopolymer mixtures and therefore presents a viable option for utilizing mineral wool waste in alkali activated materials.

2 Materials and methods

Precursor analysis

To aid in the geopolymer mix design, the chemical compositions of the fly ash and rockwool waste (Paroc Panel Systems, production waste) were first analysed, **Error! Reference source not found.** The chemical composition of the precursors was determined with X-ray fluorescence (XRF) from a melt-fused tablet. Rockwool composed of 42% SiO_2 and 16.6% Al_2O_3 , giving natural $\text{SiO}_2/\text{Al}_2\text{O}_3$ -ratio of 2.53. Aluminum and silicon, which are responsible for the geopolymerization, account for 58.6% of the total composition in rockwool. Fly ash was from pulverized coal combustion, with 2.5 % loss on ignition at 800 °C, and median particle size of 15 μm .

Table 1: Chemical composition of the starting waste materials, in weight percentages as determined by XRF.

	<i>Rockwool</i>	<i>Fly ash</i>
CaO [%]	14,7	4,3
SiO ₂ [%]	42,0	58,0
Al ₂ O ₃ [%]	16,6	21,7
Fe ₂ O ₃ [%]	11,3	5,8
Na ₂ O [%]	1,6	1,5
K ₂ O [%]	0,5	2,4
MgO [%]	12,2	2,1
P ₂ O ₅ [%]	0,1	0,9
TiO ₂ [%]	0,9	1,0
SO ₃ [%]	0,03	0,4
Cl [%]	0,04	0,04

In order to assess the reactivity of the raw materials a selective dissolution method [28–30] was utilized. With this method it is possible to determine the fraction of each component that is available for hardening reactions (reactive fraction) [31]. The reactive calcium CaO, silica SiO₂ and aluminium Al₂O₃ were determined as an amount of soluble in ethylenediaminetetraacetic acid (EDTA, 0.025 M) and triethanolamine (TEA, 0.017 M) solution having pH of 11.6 ± 0.1. The dissolution was performed in room temperature, stirring for 30 minutes. Solid/liquid ratio in the dissolution procedure was 1:105 (2.5 g sample, and 262.5 ml liquid). The solution was then filtered using GF/C filter paper, washed seven times with deionized water, and three times with ethanol. Solid residue was then dissolved further in order to reduce the error from formed precipitates in the first step: residue was stirred in 100 ml of 5 % HCl, for three hours in room temperature, filtered and rinsed with water. The contents of CaO, SiO₂ and Al₂O₃ in the solution were determined using the inductively coupled plasma (ICP) technique (ICP-OES Thermo Scientific iCAP 6000 series w/ quartz glass torch).

XRD analyses was performed to the starting materials (mineral wool waste and fly ash), and to the final geopolymer materials. The preparation steps differed slightly: the geopolymer samples were simply homogenized manually in an agate mortar, and the mineral wool waste was ground in a Retsch Cryomill with 25

Hz frequency, 3 min grinding time and 2.5 min pre-cooling time with nitrogen. Identification of the main crystal phases of powdered samples were made with Siemens 5000 X-ray diffractometer with CuK α radiation (40 mA and 40kV) and graphite monochromator. Step interval, integration time and angle interval used were 0.04°/step, 2.5 s/step, and 10-70°, respectively. ICDD-database was used for identification of crystal phases [32].

For Field Emission Electron Microscope analysis (FESEM, Zeiss Ultra Plus) geopolymer samples and mineral wool waste were attached on a carbon tape and coated with carbon. Acceleration voltage was 5 kV and beam current 9.95 nA.

Geopolymer preparation

Geopolymers were prepared by first mixing liquids, then adding fly ash, sand and finally rockwool waste in a small laboratory mixer (Kenwood Titanium). The purpose of adding sand was to aid in dissolution and breaking of the mineral wool fibres – the sand grains act as grinding media delivering impact to the fibres. Tap water and sodium aluminate were mixed and cooled beforehand to avoid the exothermal reaction during alkali activation. Rockwool waste was added in roughly ten batches during 40 minutes to enable the dissolution of the fibres while mixing. If rockwool was added all at once, proper mixing was impossible due to the dryness of the resulting paste. Therefore, by adding the rockwool gradually and letting it dissolve and break in the alkaline environment, proper mixing was achieved, see **Error! Reference source not found.** for the schematic illustration of the mixing procedure.

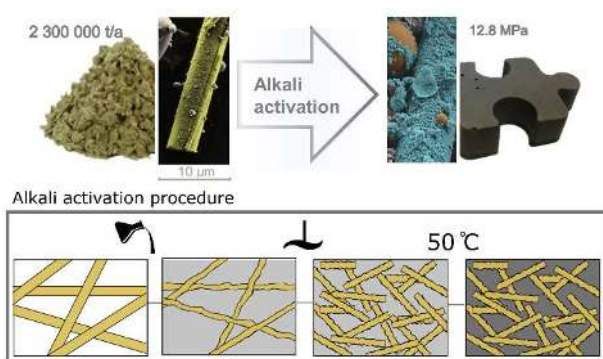


Fig. 2 Alkali activation process used for waste rockwool fibers. Above: The visual appearance of the alkali activated rockwool, including false colored microscope images. The digital false coloring was done for clarity, fly ash can be seen as spherical brown particles, while the formed geopolymer is cyan in color. Below: a flowable paste was formed by combining the dissolution of rockwool fibers in high pH and mechanical forces of mixing. Geopolymers were then cured at slightly elevated temperatures

After mixing, the paste was poured into 25 mm by 25 mm plastic cylindrical moulds, sealed watertight and cured at 80 degrees Celsius for 48 hours. Samples were demoulded after heat treatment, and kept sealed in room temperature before further analysis.

Five different mix designs were tested, with $\text{SiO}_2/\text{Al}_2\text{O}_3$ -ratio ranging from 1.8 to 3.8, and the amount of water was kept constant (Table 2).

Table 2: Geopolymer mix designs, and the resulting $\text{SiO}_2/\text{Al}_2\text{O}_3$ -ratio, calculated using the selectively soluble fractions. In the geopolymer mix designs, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was varied by adding sodium aluminate (13404 Sigma-Aldrich), while the amount of Na ions was adjusted by the amount of sodium hydroxide (5 M concentration). The total amount of water in each of the composition, taking into account water in sodium hydroxide solution, was constant (39.2 g).

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	RW-only*
Rockwool waste [g]	35	35	35	35	35	50
Filler (sand) [g]	15	15	15	15	15	
Fly ash [g]	50	50	50	50	50	
Added water [g]	20.7	25.3	30	34.6	39.2	32.4
NaOH 5M [g]	24	18	12	6		24
Sodium aluminate [g]		5	10	15	20	
Resulting $\text{SiO}_2/\text{Al}_2\text{O}_3$ [molar ratio]	3.8	3.0	2.5	2.1	1.8	3.6

In addition rockwool-only geopolymer was prepared for XRD and SEM observations in order to study the resulting reaction products (**Error! Reference source not found.** and **Error! Reference source not found.**).

For the unconfined compressive strength measurements, the top and bottom ends of the specimens were sanded flat by sand paper, and the unconfined compressive strength was measured using Instron 8500.

Compressive force was increased at 2.4 kN/s until failure, and the maximum force was used to calculate the compressive strength. The average of three specimens was calculated, and the error bars show standard deviation in each direction.

The leachable hazardous elements were tested on a rock wool-only geopolymer sample. The sample was prepared by mixing 140 g of pulverised rock wool with 63 g of sodium aluminate solution (14.3 wt% sodium aluminate (Sigma Aldrich), 22.2 wt% NaOH (VWR Merck) and 63.5 wt% H₂O). Geopolymer paste was cast into cylindrical mould and hardened in oven (50 °C) for 4 days and then 24 days in room temperature in a plastic bag. After one year the leachable concentration of hazardous components from the rock wool geopolymer sample were determined by the method described in SFS EN 12457-2.

3 Results and Discussion

Mineralogy and microstructure

Rockwool proved to be excellent geopolymer precursor material due to its high solubility. Selective solubility test was conducted on the precursor materials at pH 11.6, and rockwool was almost twice as soluble as fly ash (Fig. 3). The solubilities obtained by the selectively soluble method most likely underestimate the solubilities in the geopolymer reaction, where pH is higher, up to 14.

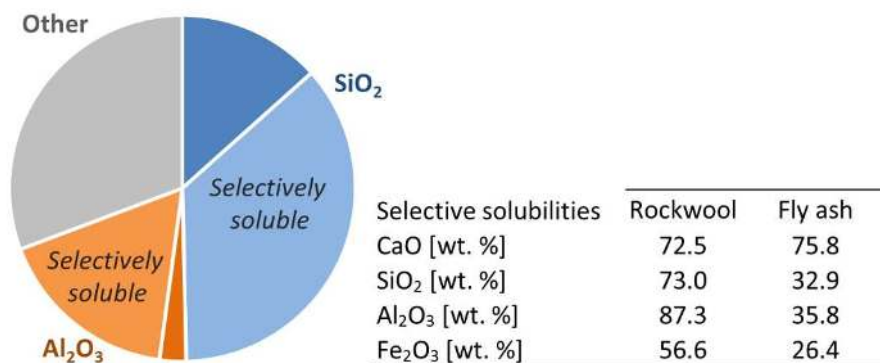


Fig. 3 Selective solubilities of precursor materials at pH 11.6. Pie chart showing the selectively soluble portion of the rockwool

The solubility of the material was also evident in the mixing behaviour of the geopolymer pastes containing rockwool fibres; the workability of the solution increased considerably during mixing. This change in workability is most likely caused by a decrease in the length of the individual mineral fibres, which are broken down in the high pH of the solution. Fiber length has been shown to affect solution viscosity to a high degree [33]. This dissolution behaviour was successfully utilized in processing: by adding the mineral wool in multiple batches and letting the fibres dissolve before adding more. In contrast, if the fluid and mineral wool was mixed all at once, the resulting mix was a wet fiber mat, which could not be mixed effectively. This processing lead to geopolymer formation as well (Fig. 4 “rockwool-only geopolymer”), however it lead to soft material with low integrity (Fig. 5 d).

Therefore, because the selective solubility of mineral wool is very high (Fig. 3), and the workability of the geopolymer paste increased drastically over time, it is safe to assume that the mineral wool fibres are dissolved and broken during the synthesis steps. The dissolution is not complete, since fibres can still be seen in the SEM images of the final geopolymer (Fig. 5 b and c).

The geopolymer gel is difficult to characterize, the composition of the gel is not constant, and therefore XRD analysis is the go-to analysis when analysing geopolymer gels. The presence of geopolymer can be seen in XRD diffractogram as a “halo” around 29 degrees, and crystalline peaks result from the zeolite phases.

In order to assess the mineralogical composition of the raw materials, XRD analysis was conducted as well, revealing the crystalline structures. XRD findings corroborated the solubility data: insoluble crystalline phases, quartz and mullite were present in the fly ash sample, while rockwool waste was completely amorphous, showing no visible peaks and a broad halo around 30° 2θ (**Error! Reference source not found.**).

Analysis was carried out on the geopolymer samples as well, where some crystalline phases were present, and a halo at 27-29° 2θ, which can be attributed to geopolymerized amorphous gel [18]. The crystalline or semi-crystalline phases formed by alkali activation of rockwool with fly ash were mostly sodium-aluminate-

silicate-hydrate (NASH) which is the main reaction product in alkali-activated systems, and aluminate-substituted calcium silicate hydrate (CASH) gel, which is a binding phase of hydrated Portland cement [34].

These same CASH and NASH phases were also present in the rockwool –only geopolymer, clearly showing that mineral wool can be used as a geopolymer precursor. To our knowledge, this is the first time geopolymers have been prepared with mineral wool as the main precursor material.

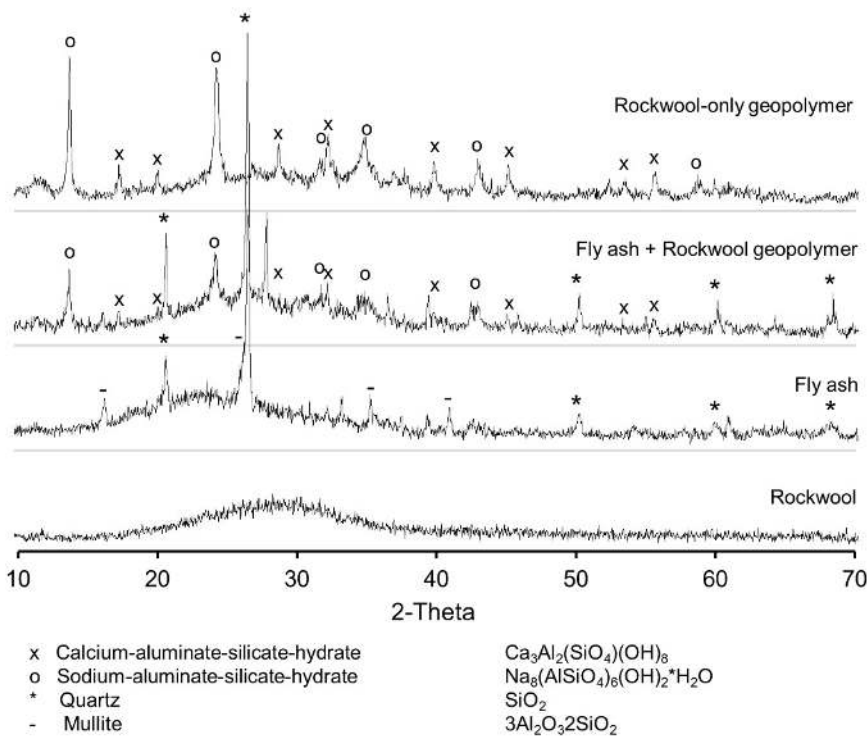


Fig. 4 Mineralogical characterization of the raw materials and formed geopolymer

Rockwool sample also contained 12.2 % MgO and 11 % Fe₂O₃, which have been suggested to take part in the geopolymer reactions [35, 36]. However, the geopolymer product did not seem to include reacted magnesium, which have been reported to consist of hydrotalcite, Mg₆Al₂(CO₃)(OH)₁₆·4(H₂O) [35]. However, it may be in amorphous form, in which case it cannot be seen in XRD gram, so it cannot be ruled out.

To further assess the microstructure of the geopolymerization, SEM images were acquired of the rockwool before and after alkali activation with fly ash (**Error! Reference source not found.**). The diameter of the rockwool fibers is roughly 10 micrometers before the geopolymerization (**Error! Reference source not found.a**), and after the reaction some undissolved fibers can be found. The SEM image of the fly ash rockwool fracture surface reveals a continuous matrix with partly undissolved fibers and fly ash particles present (**Error! Reference source not found.b**). In higher magnification of the same geopolymer a layer of the reaction products can be found covering the unreacted fly ash particles and rockwool fibers (**Error! Reference source not found.c**).

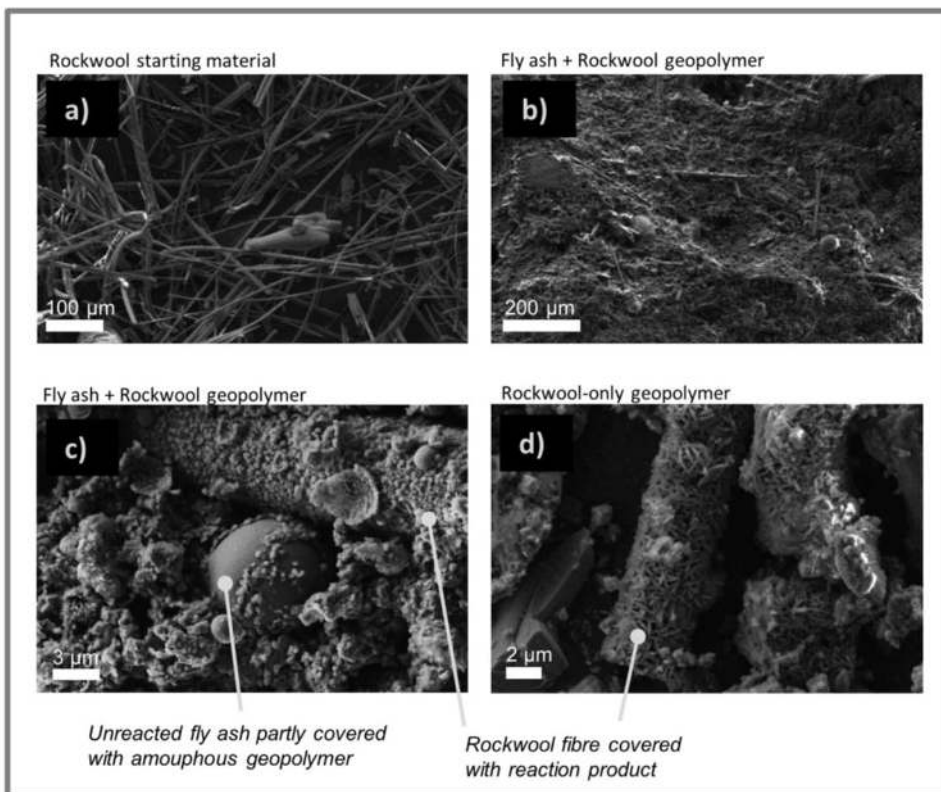


Fig. 5 Scanning electron microscopy pictures of the rockwool geopolymers

Additionally rockwool -only geopolymers were prepared, however with higher liquid to solid (L/S) ratios. This method was not successful in creating monolithic samples, and the compressive strength was on the order of 1 MPa. Microstructural characterization revealed however, that partial dissolution took place (**Error! Reference source not found.**d) and the reaction products were mainly crystalline, which should be expected for L/S ratios due to more extensive zeolite formation (**Error! Reference source not found.**). The reaction products comprised of calcium-aluminate-silicate-hydrate and sodium-aluminate-silicate-hydrate.

Leaching tests

In order to test the feasibility of the geopolymerized material in construction applications, the leachable hazardous elements were tested on a rock wool-only geopolymer sample (Table 3). The only element that was leachable in notable concentration was vanadium. Vanadium can exist as oxyanionic-species under alkaline conditions and has been observed to leach from coal fly ash-based geopolymers [37]. The composition and activator was not optimized for the geopolymerization, and it is expected that the leached concentrations can be lowered considerably by optimizing the alkali-activation protocol.

Table 3: Leached concentration of hazardous components measured by SFS EN 12457-2 protocol.

<i>Element</i>	<i>Leachable concentration (mg/kg)</i>
<i>As</i>	<i><0.15</i>
<i>Ba</i>	<i>0.18</i>
<i>Cd</i>	<i><0.02</i>
<i>Cr</i>	<i>0.57</i>
<i>Cu</i>	<i>0.76</i>
<i>Mo</i>	<i><0.05</i>
<i>Ni</i>	<i>0.26</i>
<i>Pb</i>	<i><0.15</i>
<i>Sb</i>	<i><0.16</i>
<i>Se</i>	<i><0.17</i>
<i>V</i>	<i>23.3</i>

Zn	<0.1
Hg	<0.002
DOC*	2940
F	<20

Mechanical properties

To assess the mechanical qualities of the formed geopolymers, their unconfined compressive strength was measured after 28 days of curing in ambient temperature, and the results can be seen in Fig. 6. The highest compressive strength and the highest bulk density were both achieved with $\text{SiO}_2/\text{Al}_2\text{O}_3$ -ratio of 2.47, that contained 33% rockwool waste and 47% fly ash, resulting in 12.8 MPa compressive strength. There was no clear correlation between the bulk density and compressive strength (see Supplementary Information, Fig. S1). The bulk densities of the resulting geopolymer pastes varied between 1.33 and 1.59.

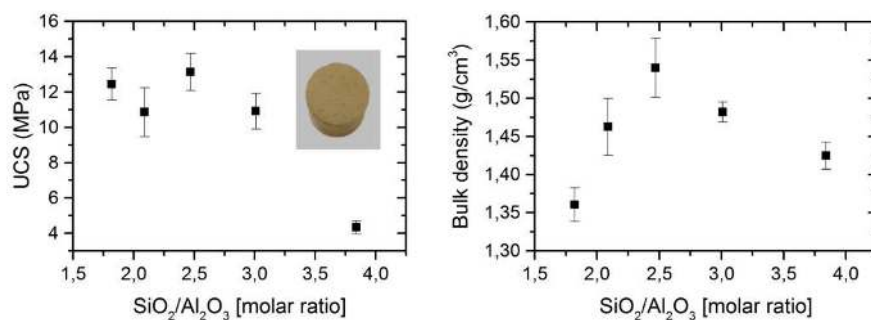


Fig. 6 Mechanical properties of the geopolymer composites. Unconfined compressive strength as a function of the soluble $\text{SiO}_2/\text{Al}_2\text{O}_3$ -ratio (left) and the bulk density (right). Inset: Optical image of the sample with the highest compressive strength after demolding

Rockwool typically consists of 96-98% inorganic material, and the rest is an organic binder, typically urea modified phenol-formaldehyde binder [38]. This organic binder does not seem to negatively effect the alkali-activation, however its fate in the final product is unknown. This issue is very important when considering the

reuse of mineral wool as geopolymer precursor, especially the possibility of volatile emissions. Further investigation is required to determine the VOC emissions of the geopolymers.

4 Conclusions

The object of this work was to develop a method for utilization of mineral wool waste as a geopolymer binder raw material, with high fraction of mineral wool waste in the mix design. Using the newly described method, geopolymers with excess of 12 MPa compressive strength were synthesized, with 33% rockwool and 47% fly ash inclusion. The resulting geopolymer paste was achieved with H₂O/dry mass –ratio of 0.40, and had a SiO₂/Al₂O₃ -ratio of 2.47. The geopolymerisation was verified using X-ray diffractometry, and the reaction products included calcium alumimun silicate hydrate and sodium aluminum silicate hydrate, which are the main binding phases of alkali activated systems with calcium. The same reaction products were present in pure rockwool geopolymer and in geopolymer prepared using fly ash and rockwool as precursors.

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