High strength one-part alkali-activated slag blends designed by particle packing optimization

Priyadharshini Perumala,⇑ Harisankar Sreenivasan, Tero Luukkonen, Anu M. Kantola, Ville-Veikko Telkki, Paivo Kinnunen, Mirja Illikainen

A Fibre and Particle Engineering Research Unit, University of Oulu, Pentti Kaiteran katu 1, 90014 Oulu, Finland
B NMR Research Unit, Faculty of Science, University of Oulu, P.O. Box 3000, 90014 University of Oulu, Finland

HIGHLIGHTS

- One-part alkali activated binary and ternary mortar blends are designed by optimizing the particle packing.
- Distribution modulus to be chosen based on the mix composition for maximum packing density.
- A record high strength of 145 MPa is achieved with ternary blend with slag, silica fume and phyllite dust.
- Addition of silica fume resulted in cross-linked C-A-S-H and N-A-S-(H) formation.

ARTICLE INFO

Article history:
Received 28 September 2020
Received in revised form 24 March 2021
Accepted 14 June 2021

Keywords:
One-part alkali activated material
Strength
Particle-packing
Ternary blend

ABSTRACT

This paper focuses on the development of high-strength and eco-friendly one-part (i.e., dry-mix) alkali-activated mortar with ground granulated blast furnace slag as the main precursor. In addition to slag, phyllite dust and silica fume were used as co-binders in binary and ternary blends to improve mechanical properties. Particle packing optimization was employed for the mix proportioning to achieve a compact matrix skeleton. The results revealed that a 10% increase in mortar strength was gained after adjusting the particle packing and an additional 20% increment was observed after blending the slag with other mineral admixtures. Ternary blend with all three binders achieved a mortar compressive strength value of 145 MPa (at 28 d age), which is the highest strength reported in one-part alkali-activated materials. Additionally, ternary blends present potential economic benefits because of their ability to replace slag with lower-cost industrial side streams.

1. Introduction

Alkali-activated binders have been gaining popularity in the construction industry owing to their potential to cut down CO₂ emissions [1–3]. However, they are not yet widely applied due to issues related to corrosive alkali-activator solutions and the requirement of elevated temperature curing in some of the alkali-activated materials (AAM) [4,5]. In this regards, one-part AAMs have recently gained a significant amount of attention since they follow similar mixing procedures as that of ordinary Portland cement (OPC) concrete [6]. However, the concept of “just-add-water” AAMs was initially developed by Kühl [7] as early as 1908 for producing slag-based AAM. Later, the technology was adopted in many studies and found to be useful, especially for on-site construction activities [8]. One-part systems are not being as widely used in construction projects as two-part AAMs, which were recently applied in the construction of the University of Queens-

https://doi.org/10.1016/j.conbuildmat.2021.124004
0950-0618/© 2021 The Author(s). Published by Elsevier Ltd.
This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).
land's Global Change Institute (2013, Australia) and the Too-woomba Well camp Airport (2014, Australia), as examples. Potential reasons for this include the hygroscopic nature of some one-part activators, and less scientific research in the area [6]. Nevertheless, there have been attempts to commercialize one-part AAMs as well [9–11]. The precursor materials of AAM, which are usually industrial side streams, define the properties of the resulting matrix irrespective of the preparation method. Mainly, it can be a high- or low-calcium system based on the chemical composition of the ingredients used [12]. For example, blast furnace slag is rich in calcium, which results in the formation of calcium silicate hydrate (C-S-H) or calcium alumino-silicate hydrate (C-A-S-H) as a major binder matrix, whereas low-calcium precursors, such as metakaolin, result in the formation of binder phase sodium alumino-silicate hydrate (N-A-S-(H)) [12–14]. The product phase of alkali-silicate activation of Ca-rich GGBFS consists of poorly crystalline aluminum-substituted C-A-S-H type gel along with alkali alumino-silicate (hydrate) phase (N-A-S(-H)) gel [15]. C-A-S-H gel has two kind of units: cross linked as well as non-cross linked toborerite-like units (Fig. 1). The cross-linked unit consist of mainly Q3 silicate species with bridging formed by Al[IV] in q3 site. The noncross-linked unit consists of mainly Q2 silicate species with Al[IV] in q2 site. The (N-A-S(-H)) gel consists of mainly Q2(4Al) and Q3(3Al) silicate species with Al[IV] in q3 sites.

The blending of two binders of different composition could result in the stable co-existence of C-(A)-S-H and N-A-S(-H), which is favorable for cross-linking and stronger bonds, which in turn bridge the gap between different hydrated phases and unreacted particles [16]. Another benefit of using slag is its ability to help avoid elevated temperature curing [17]. Hence, one-part AAMs with slag can be viewed as a material with potential to partially replace OPC-based materials [18,19]. However, the presence of slag results in certain negative effects, such as, reduction in workability due to the effect of free lime that accelerates hardening and high-magnitude shrinkage by the fine pore size distribution [20,21]. This can be managed to some extent with superplasticizers or other advanced admixtures in the case of one-part alkali-activated slag mortar [22,23]. The workability of the material can also be improved by using blended binders that compensate for negative effects; for example, a material such as fly ash with its spherical shape helps in improving flow properties [24].

In this study, four different mixes with slag were studied: only slag, binary mixes (with slag and silica fume or phyllite dust) and ternary mix (with all three binders) on mortar properties. The particle packing optimization method in mix design was applied to improve the packing of different binders based on their particle size. The alkali activator (solid sodium silicate, SiO2/Na2O = 0.9) was co-grinded with slag and all of the four mortar mixes were prepared as one-part AAMs. The aim of the study was to maximize the compressive strength of one-part AAMs and shed light on the effect of blending different materials in slag-based AAM and the influence of particle packing in blended AAM.

Fig. 1. The schematic representation of cross-linked and noncross-linked C-(N)-A-S-H units [15].

2. Experimental program

2.1. Materials

Ground granulated blast-furnace slag (GGBFS) with the specific gravity of 2.95 was procured from Finnsementti, Finland. The GGBFS was co-grinded with 10% of anhydrous sodium metasilicate (molar SiO2/Na2O = 0.9, supplied as 1 mm granules by Alfa Aesar, Germany) in a ball mill for 30 min to attain a d50 value of 9.75 μm and to facilitate high strength one-part alkali activation. Earlier research well documented the effectiveness of co-grinding and fineness on strength characteristics of GGBFS based two-part alkali activated cements [25]. Commercially available granulated silica fume (tradename Parmix-silika, Fescon Ltd., Finland) with the following specifications as reported by the manufacturer: SiO2 > 85%, Cl < 0.10%, Na2O equivalent < 3.0%, specific surface area 15–35 m2/g, and activity index > 100%, was obtained. The d50 Value of granulated silica fume before milling was ~ 200 μm which was milled for 10 min in a mortar grinder (Retsch RM 200, Germany) to a d50 value of 23.12 μm. Phyllite dust, a powder waste generated while manufacturing roof tiles, was acquired from a local industry in Finland (density = 2.88 g/cm3 and d50 = 196.77 μm), CEN standard sand (Normensand, Germany) with a density of 2.68 g/cm3 and passing 2 mm, was used as aggregate material. Two different size fractions of the aggregate, passing through 500 μm (fine sand) and retained in 500 μm (coarse sand), were obtained from the standard sand. The chemical composition of the binder materials used in this study was determined with AxiosMax (PANalytical, UK) XRF spectrometer and is presented in Table 1. Secondary electron images of the binders from a scanning electron microscope (Zeiss Ultra Plus, Germany) are depicted in Fig. 2. The secondary particle of milled silica fume is magnified to show the agglomerates of smaller primary particles in the Fig. 2. (b). The particle size distributions (PSD) by laser diffraction (Beckman Coulter LS 13320, USA), which were obtained by dispersing the materials in isopropanol, are provided in Fig. 3. PSD results revealed that co-grinded slag (with sodium silicate) was the finest material, followed by silica fume (secondary agglomerates) and phyllite dust. Three materials of different d50 values were chosen to be the binders for the ternary blends.

2.2. Mix design

It has long been known that the performance of concrete could be improved by designing the mixture proportion in a manner that reduces water content and minimizes voids. Alternatively, optimizing the content and proportion of ingredients for better packing density in an economical manner also improves the strength of the concrete. Many theories related to packing have been established, beginning with the Fuller curve, which mainly focuses on aggregate packing. The distribution modulus (Q) was introduced to adjust the compaction and packing density of individual ingredients based on their gradation curve as depicted in Eq. (1) [26].

\[
P(d) = \left(\frac{d}{d_{\text{max}}}ight)^Q
\]

Here, P(d) is the cumulative percent finer than d (the particle diameter), and dmax is the maximum size of the particle used in the mixture. Andreasen and Andersen proposed that for maximum packing density the Q value can vary between 0.33 and 0.50 [27]. However, Q value can be altered to achieve optimum packing density for materials of different size fractions. The Q value should be carefully chosen as it can also result in negative effects, such as segregation or higher viscosity with an excessively fine content. However, the need for d50 was eventually recognized, as the
The smallest particle size also plays a role in the compact packing of the mixture. Hence, the modified Andreasen model was proposed as given in Eq. (2) [28] and used in various mix design concepts [29,30].

\[ P(d) = \frac{d^q - d_{\text{min}}^q}{d_{\text{max}}^q - d_{\text{min}}^q} \quad (2) \]

Particle packing techniques for mix design involves selection of materials of appropriate size and quantity that can result in maximum packing density. The solid volume of particles in a unit volume (packing density) can be optimized using the curves given in Eqs. (1) and (2). This can be done by optimizing the mix composition by adjusting the Q value or the expected workability, as has been done previously [27,31,32]. Here, instead, the proportions of mix ingredients were adjusted to match the PSD curve with a fixed Q value. The EMMA mix analyzer (Elkem, Norway), a commercial software [33], was used and the mixture proportion was optimized to fit in two different Q values (0.25 and 0.3) in the modified Andreasen model. Four different mixes of slag-based alkali-activated mortar with binary and ternary blends (aggregate to binder ratio: 2) were designed as depicted in Table 2.

Table 1
Chemical composition of binders used.

| Oxide [%] | Na₂O | MgO | Al₂O₃ | SiO₂ | P₂O₅ | SO₃ | K₂O | CaO | Fe₂O₃ | TiO₂ | LOI (525 °C) | LOI (950 °C) |
|-----------|------|-----|-------|------|------|-----|------|-----|-------|------|--------------|--------------|
| GGBFS     | 0.51 | 10.24 | 9.58 | 32.33 | 0.01 | 4.01 | 0.53 | 38.51 | 1.23 | 2.21 | –            | 0.46         |
| Silica fume | 0.18 | 0.35 | 0.23 | 94.25 | 0.01 | 0.13 | 0.56 | 0.78 | 0.84 | – | 1.69 | 2.31         |
| Phyllite dust | 2.06 | 0.81 | 8.96 | 71.91 | 0.08 | 0.26 | 2.29 | 9.01 | 2.07 | 0.25 | 2.20 | 3.40         |

Fig. 2. SEM micrographs with 2000X magnification of (a) GGBFS (b) Silica fume (c) Phyllite dust.

Fig. 3. Particle size distribution of materials used in the mix design.
Raw materials (binder and aggregate) were mixed dry in a Hobart mixer for 3 min, and the mixing was continued for another 2 min after adding tap water. Three different water/binder (W/B) ratios (0.25, 0.30 and 0.35) were used in this study to investigate the effect of water content on the designed mixtures as in Table 2. Lignosulphonate (WRDA 90D) was used as a superplasticizer with a dosage of 0%, 0.5% and 1% binder for the water/binder ratio of 0.35, 0.30 and 0.25, respectively. The fresh mortar was then cast as prismatic (40×40×160 mm) or cubic (50×50×50 mm) specimens as given in the schematic diagram (Fig. 4). Compaction was ensured with the help of a jolting table (2×60 shocks, 1 shock/s). The specimens were closed in a plastic bag and cured in a closed chamber at a temperature of 20 °C and 100% humidity.

2.3. Test methods

2.3.1. Fresh properties

Paste samples were prepared by eliminating the aggregate content and used for measuring the heat evolution during alkali activation process. The Tam Air isothermal calorimeter (TA instruments, USA) with an 8-channel was used for this purpose, in accordance with ASTM C 1702 [34]. The measurements were conducted at 20 °C for 72 h to mimic the actual curing conditions. Freshly prepared mortar with different mix proportions (Table 2) was studied for its flow characteristics: Workability as a percentage of spread was measured with the flow table as per ASTM C1437 [35].

2.3.2. Strength characteristics

Triplets of the prism specimens (40×40×160 mm) were used to measure the flexural performance of each mix with a three-point bending test in accordance with EN 196–1 [36]. The test was performed under deflection control at a deflection rate of 0.6 mm/min, and the load (F) was measured using a load cell with a capacity of 100 kN in the Roell Z100 (Zwick, Germany) testing machine.

The broken pieces of the prism after the three-point bending test were used to determine the compressive strength of the mix as per EN 196–1 standards [36]. Hence, six specimens for each mix were tested with the controlled displacement of 1.8 mm/min, and the load was measured using the Toni Technik testing machine with a 3000-kN capacity.

2.3.3. Porosity and water absorption

Cubic specimens were used for the purpose of measuring the water absorption, apparent density, and porosity of the mixes. Test procedure was followed as per EN 1936: 2006, with the slight modification of specimens being dried in an oven at a temperature

![Fig. 4. Mortar preparation and testing procedure.](image)
of 105 ± 5°C instead of the specified 70 ± 5°C for fast drying. Specimens were dried until a constant mass (md) was reached. The dry specimens were then evacuated in low pressure of 2.0 ± 0.7 kPa in a desiccator for 2.0 ± 0.2 h. This procedure was followed to remove the air from the open pores of the specimens, and after this, deionized water was introduced to immerse and saturate the specimens for 24 ± 2 h. The weight (mh) of the specimen under water was measured using a wire basket suspended from the weighing balance and immersed in water. The specimens were wiped with damp cloth to determine the surface saturated weight (ms). The apparent density (ρb, kg/m³), open porosity (Po, %) and water absorption (W, %) with an average from three specimens are derived from Eqs. (4), (5) and (6), respectively, where ρh is the density of water, which is 998 kg/m³ at 20°C.

\[ \rho_b = \frac{m_d}{m_h - m_b} \times \rho_h \]  
(4)

\[ P_o = \frac{m_o - m_d}{m_h - m_b} \times 100 \]  
(5)

\[ W = \frac{m_h - m_d}{m_h} \times 100 \]  
(6)

2.3.4. Microstructure analysis

Mortar samples from strength testing were preserved to study the microstructural development of alkali-activated slag with binary and ternary blends. Small chunks of mortar samples were placed in acetone for 3 days to stop hydration by solvent exchange, and the samples were placed inside the desiccator until imaging. The samples were cast in epoxy resin and polished with Struers MD Piano 500, 1200 and 2000. Carbon coating was employed on the samples to avoid the charging effect in the electron microscope. A field emission scanning electron microscope (Zeiss Ultra Plus) with an energy dispersive spectrometer was used to capture back-scattered electron images with an accelerating voltage of 15 kV and working distance of 8 mm.

2.3.5. Chemical structure and characterization

Structural characterization of alkali activated mixes were performed with the powdered paste samples (cured for 28 days at 20°C and 100% relative humidity) made with a water-binder ratio of 0.30 and distribution modulus (Q) of 0.30 (samples as used in calorimetric study).

X-ray diffraction (XRD) was used to study the presence of amorphous and crystalline phases in the raw materials (binders) and formation of different phases after activation with sodium silicate present in the co-grounded slag in mixes with binary and ternary blends. Rigaku SmartLab 9 kW diffractometer with Co-Kα radiation (Kα1 = 1.78892 Å; Kα2 = 1.79278 Å; Kβ1/ Kβ2 = 0.5), at a scan rate of 3°/min and a 20 ranging from 5° to 120°, was employed. The ICDD PDF4 database was used in phase identification using the X'pert HighScore Plus software (PANalytical software).

Bruker Vertex 80v spectrometer was used to capture the Infrared Fourier transform (FTIR) spectra of the binders and alkali-activated pastes. A range of 400 to 4000 cm⁻¹ and 40 scans with a resolution of 1 cm⁻¹ were used for this process. The 27Al and 29Si NMR spectra were obtained on a Bruker Avance III 300 spectrometer operating at 78.24 MHz for 27Al and 59.65 MHz for 29Si. For the MAS experiments, the samples were packed into 7 mm zirconia rotors, and rotation frequency of 7 kHz was applied. For 27Al, 2048 scans were accumulated with a repetition rate of two seconds. No proton decoupling nor cross polarization was used. The chemical shifts were referenced to Al(NO₃)₃ set to zero ppm. For 29Si, 8192 scans were accumulated with a repetition rate of three seconds. The chemical shifts were referenced to TMS (tetramethylsilane) set to zero ppm.

3. Results and discussion

3.1. Fresh properties

3.1.1. Isothermal calorimetry

The heat flow curves of different mixtures are depicted in Fig. 5. Mixtures of different blends with same Q value (0.30) and W/B ratio (0.25) were chosen to study the effect of binary and ternary blending on alkali-activated slag (Fig. 5 (a)). The calorimetric curve exhibited two peaks. Peak 1 corresponded to the exothermic reaction due to the immediate adsorption of alkali solution on the surface of binders when it came in contact with water (wetting process) and also corresponds to the heat evolved from the dissolution of sodium silicate co-grounded with GGBFS. This appeared to be the case for all four different mixtures. The reaction rate of GA mix was higher than other mixtures in Stage 2 (Peak 2), which corresponded to the breaking of alumino-silicate precursors into oligomers. This effect indicates that the polymerization of slag occurred at a faster rate compared to that of binary and ternary blends. The presence of secondary agglomerates in silica fume in binary and ternary blends also partly explains the later appearance of the second peak, as OH⁻ released by sodium silicate can be consumed for dispersing and depolymerizing silica fume.

The peak heat flow of alkali-activated binary blend with silica fume (GSA) was depressed while the alkali-activated binary blend with phyllite dust (GDA) displayed only slight depression as that of GA. This may be related to the fact that phyllite dust contains alumina (Al₂O₃) content equivalent to slag, which is known to affect the initial setting and strength development of alkali systems [37, 38]. However, the phyllite dust added here was not pretreated and hence is expected to be a nonreactive filler. The delay and drop in peak 2 with GA mix is attributed to the contribution of silica fume to the silica modulus (SiO₂/Na₂O) which slows down the reaction, reportedly due to the reduction in alkalinity of the system [39].

The calorimetric curve of the alkali-activated ternary blend (GDSA) produced with different water content exhibited a similar trend with the previous curves with two reaction stages (Fig. 5 (b)). The highest peak occurred with the mix with the lowest W/B ratio. Higher water content dilutes the OH⁻ ion concentration, which in turn slows down the reaction rate. In addition, higher water content hinders the polycondensation of silica and/or aluminosilicate oligomers as the reaction involves the release of water [40]. The experimental results clearly demonstrate that the water content of the mix affects the initial reaction kinetics of one-part alkali activated materials.

3.1.2. Flow characteristics

The flow properties measured by the spread percentage of alkali-activated slag-based blends are shown in Fig. 6. Spread percentage was higher for a Q value of 0.25 (Fig. 6 (a)) than for a value of 0.30 (Fig. 6 (b)). As Q approached a lower value, the gradation became finer which improved the flow. This may be related to the mix design adopted in this study possessing a particle packing method that fitted better finer gradation at lower distribution modulus values. This view can be justified by the increase in the proportion of finer aggregate (<500 μm) for the mixes designed with Q as 0.25 (Table 2). These results are in agreement with earlier findings of positive effect of particle packing on rheological properties, owing to the lower interparticle friction [41]. However, GA mix gives the lowest spread percentage compared to the binary or ternary blended mixes, irrespective of the Q value adopted.
Despite the irregular shape of phyllite dust (Fig. 2(c)), larger particle size and lower surface area helped in reducing the water demand in the binary mix GDA. Whereas silica fume is known to act as a superplasticizer by surface adsorption and repulsion [42], which is also the case with GSA mix in the present study. This may be the reason for the superior behavior of binary and ternary blends compared to the GA mix with only slag.

As a general trend, percentage spread increased when the W/B ratio was increased from 0.25 to 0.35; however, there were also exceptions. With a Q value of 0.30, GA mix followed a similar trend, whereas other mixes did not follow any specific pattern. Referring to the mix ratio (Table 2), the proportion of additional binders to the GGBFS varies with the Q value to fit in the packing model (Eq. (2)). For instance, the proportion of phyllite dust increased from 0.12 to 0.23 when Q value varied from 0.25 to 0.3. With the raise in the coarser proportion of the binder blend, mix with phyllite dust (GDA) exhibited very low spread values at lower W/B ratios (0.25 and 0.3). The reduction in the workability of the mix with phyllite dust can be attributed to the irregular shape of the particles (Fig. 2(b)), which increased the water demand to maintain the fluidity of the mix. However, spread percentage improved almost 3 times at a W/B ratio of 0.35 indicating the need for a minimum water content to maintain the workability while using phyllite dust as a co-binder. On the contrary, mix with silica fume (GSA) performed better than other mixes even at a lower W/B ratio of 0.25, irrespective of the Q value used. For instance, in Fig. 6(a), incorporation of silica fume as a co-binder with slag improved the spread percentage from 20% (GA) to 100% (GSA). Formation of colloidal silica was reported to be a reason for the positive effect of silica fume on the rheology and flow characteristics at a lower W/B ratio (0.25) [42]. With the increasing W/B ratio in GSA mix, there was slight increase in the spread percentage when the Q value is 0.25 (Fig. 6(a)) though there is no remarkable difference when the Q value is 0.3 (Fig. 6(b)). Earlier research also reported similar observation where the effect of W/B ratio on workability diminished at higher proportion of silica fume [43]. The ternary blend with the incorporation of co-ground slag, silica fume and phyllite dust (GDSA) displayed an average spread value of 120% when the W/B ratio was 0.30 (Fig. 6(b)). The presence of phyllite dust reduced the spread percentage which was compensated by the presence of other binders that helped in maintaining the flow. At a W/B ratio of 0.35, both GSA and GDSA shows a small dip in spread percentage when the Q value = 0.30 (Fig. 6(b)). Along with flowability, it is proven

![Fig. 5. Calorimetric curves of alkali activated (a) paste with different mix ingredients (b) ternary blend (GDSA) with different water-binder ratio.](image)

![Fig. 6. Flow properties of alkali activated mortar with (a) Q = 0.25 and (b) Q = 0.30.](image)
that cohesiveness of cement paste could be significantly improved by the addition of silica fume [44]. The silica fume content in GSA and GDSA mixes was reduced when the Q value was shifted from 0.25 to 0.30 (Table 2), affecting the cohesiveness of the mix at higher water-binder ratio leading to bleeding but not any improvement in spread value.

3.2. Hardened properties

3.2.1. Strength characteristics

The effect of different distribution modulus (Q value) on the compressive strength (at 28 d age) of alkali-activated binder with GGBFS, binary and ternary blends are shown in Fig. 7. For mix with only GGBFS as binder, a lower modulus value (Q = 0.25) led to a doubling of strength at lower W/B ratios (Fig. 7(a)). A similar trend was noted in mix with binary blend that contained slag and phyllite dust (Fig. 7(b)) with comparatively lower strength values. This can be explained by the lower heat that evolved during polymerization, which indicated the lower reactivity of the GDA mix compared to the GA mix (Fig. 5 (a)). For binary mix with silica fume (GSA), though lower Q value appeared to achieve better strength at a lower W/B ratio, the trend was reversed at a higher W/B ratio; that is, a higher Q value (Q = 0.30) resulted in higher strength values (Fig. 7 (c)). Alkali-activated ternary blend with slag, phyllite dust and silica fume (GDSA) provided higher strength with a higher Q value (Fig. 7 (d)). As the particle size distribution was shifted to coarser side for ternary blend (GDSA), increase in Q value resulted in compactly packed matrix. It can be inferred that mixes that contained silica fume (i.e., GSA and GDSA) appeared to display different trends compared to other mixes, which could be due to the dissolution of silica fume at different rates based on the availability of OH– ions in the system. Similar behavior has been observed when silica fume was used as an alternative silicate source and documented to be influenced by W/B ratio [19]. It is also important to mention that dissolution of slag/silica fume during activation also partially affects the particle packing.

Evolution of the compressive strength of alkali-activated mortar with slag and blended mixes at different curing age are shown in Fig. 8. Irrespective of W/B ratio, ternary blends show higher strength compared to other mixes. A previous study by the authors reported highest compressive strength of 107 MPa (W/B ratio = 0.35) for one-part AAM with slag [19]. In this present study of particle packing optimization, a mortar compressive strength of 145 MPa (W/B ratio = 0.30) was achieved at Day 28 with a one-part...
AAM ternary blend mix (Fig. 8(b)). According to a review of one-part alkali-activated materials [6] and to the best of the author’s knowledge, the obtained 145 MPa value is clearly the highest compressive strength reported in the published literature, considering also the standard specimen size used. A corresponding mortar flexural strength of 15.9 MPa was obtained for the ternary blend and is listed in the supplementary data (Table S1). It is reported in earlier studies of one-part AAM with similar composition that concrete strength could be 20% higher in comparison to mortar [45]. It should also be noted that compressive strength increased with an increase in W/B ratio from 0.25 to 0.30 and reduced with further increases for GDSA. In addition, strength increased with increasing W/B ratio for all other mixes, unlike the conventional trend followed for any concrete material, especially OPC. This result can be due to the optimum water requirement to dissolve the solid sodium silicate and other reactive Si/Al species in one-part AAMs, whereas in the two-part method, the alkali activator is introduced as a solution. However, similar observation of strength increase with W/B ratio was reported in OPC mortars containing high silica fume content (30%) and found that Abram’s generalized W/B law was not applicable to mortars with silica fume [46]. This seems to be true also for one-part alkali activated materials in the present study.

The strength variation with different mixtures were further analyzed with XRD and NMR to determine the details behind the behavior. The results of the 29Si NMR analysis of alkali-silicate activated GGBFS are displayed in Fig. 9a. The mixing of the reactants have been provided in Supplementary Fig. S1. Since the mix design involved up to 4 raw materials, it would be highly difficult to deconvolute the spectra into components representing various Qn species as well the contributions coming from unreacted raw materials. Hence, instead of comparing various product spectra on absolute terms, relative comparison is more practical in this case. It can be seen that products of compositions without addition of silica fume (GA and GDA) are dominated by Q2 and Q1 silicate species (The chemical shift range for various Qn species were obtained from literature [47–50]). This means that in these products, C-A-S-H gel is dominated by noncross-linked structures. In these cases, there was less formation of cross-linked C-A-S-H structures as well as (N-A-S(-H)) gel (due to less Q3 and Q4 silicate species). In the case of products of compositions involving silica fume (GSA and GDSA), there was a dominance of Q2 species along with consider-
able proportion of Q3 as well as Q4 species (GSA additionally has another band representing Q4 species, originating from unreacted silica fume). This means that these systems are dominated by both forms of C-A-S-H structures (cross-linked and noncross-linked) as well as (N-A-S(-H)) gel. This coexistence of C-A-S-H was consistent with the amorphous hump XRD pattern of tobermorite at 33 to 35° (Fig. 10). Additionally, GSA displayed an amorphous hump at approximately −114 ppm which corresponded to the unreacted silica fume (Fig. 9(a)). This finding suggests that there is an optimum quantity of silica fume addition beyond which it remains unreacted in the system.

The observations made so far can be used for understanding strength development in terms of product phase formation. Absence of additional silica sources led to the predominance of noncross-linked C-A-S-H structures and poor strength development for GA and GDA. Presence of additional silica sources led to the predominance of both forms of C-A-S-H structures (cross-linked and noncross-linked) as well as (N-A-S(-H)) gel and high strength for GSA and GDSA. However, it can be seen that the strength of GDSA was significantly higher than that of GSA. This can be attributed to the over dosage (beyond the optimum level) of silica fume in GSA leading to part of the silica fume remaining in an unreacted form and poor strength development when compared to GDSA.

The results of the 27Al NMR analysis of alkali-silicate activated GGBFS are depicted in Fig. 9b (those of reactants have been provided in Supplementary Information). It can be seen that products of compositions lacking silica fume (GA and GDA) have both tetrahedral and octahedral aluminum (The chemical shift range for various aluminum coordination species were obtained from literature [15,48,51–53]). The tetrahedral aluminum corresponds to predominant Al4 in the Q2 site of non-cross-linked C–A–S–H structures. The octahedral aluminum might belong to AFm phases (XRD analysis shows no AFm phases, however). It has been suggested that AFm phases can be intermixed into C–S–H structures and hence, they cannot be detected by XRD analysis [54,55]. In the case of products of compositions involving silica fume (GSA and GDSA), the tetrahedral component predominated, with a minor octahedral component (which demonstrated the predominant incorporation of aluminum in to C–A–S–H structures and (N-A-S(-H))gel. Results also suggested that the tetrahedral component in these cases shifted to lower values when compared to the first two systems. The chemical shift values of aluminum followed this order: (Al4 in Q3) > (Al4 in Q4) [47,56]. Both GSA and GDSA had a higher proportion of cross-linked C-A-S-H structures and (N-A-S(-H)) gel (having (Al4 in Q3) and (Al4 in Q4) respectively), hence providing an explanation for the downward shift of the tetrahedral aluminum component.

3.2.2. Open porosity and water absorption

The influence of Q value and W/B ratio on open porosity and water absorption of alkali-activated slag mortar and blended mortar mixtures are depicted in Figs. 11 and 12, respectively. The open porosity shows lowest value at a W/B ratio of 0.25, irrespective of mix composition except for the slag only mix (GA) (Fig. 11 (a)).
Effect of preconditioning temperature on the microstructure and thus on the absorption properties of the designed mixes, is also important to be considered here\cite{57}. However, the trend remains the same if the mixes where compared at the same preconditioning temperature (ranging from 50 to 105 °C) as stated by Pinto et al. (2018) in their study involving a wide range of water-cement ratio (0.42 – 0.6)\cite{58}.

When Q value = 0.30, the percentage of porosity reduces with increasing water content in GA and GDA, supporting the hypothesis explained for the compressive strength of one-part alkali-activated material related to the water requirement for dissolution. A similar trend was observed for water absorption (Fig. 12) and explains the influence of open porosity on the absorption properties of the AAM. The ternary blend with the highest compressive strength (GDSA, W/B ratio = 0.30 and Q = 0.30) displayed the minimum open porosity and water absorption, followed by GA, GSA and GDA (Fig. 12 (b)).

To understand this behavior of the alkali-activated mixes with optimized particle packing, the reaction between silica and alumina species and calcium compounds in an alkaline environment were examined using FTIR, and the results are represented in Fig. 13. The wider and deeper O–H stretching (2400 to 3600 cm\(^{-1}\)) and bending vibrations (1632 cm\(^{-1}\)) observed in GA and binary mixes (GDA and GSA) revealed the possible formation of 1.4 nm tobermorite type of C-S-H in the system\cite{59,60} which was consistent with the observation from XRD showing amorphous hump of tobermorite at 33 to 35° 2\(\theta\) (Fig. 10). This band was diminished with the ternary blend (GDSA); however, the main Si-O stretching occurred at 945 to 975 cm\(^{-1}\) and formation at high wave numbers indicated the presence of reaction products with lower Ca/Si ratio and co-generation of N-A-S-(H) and 3D network of zeolites. Alkali activation of slag cement resulted in the formation of C-S-H with lower Ca/Si ratio with varying crystallinity identified by the peak shift of Si-O stretching and the Ca/Si ratio was lower with the use of sodium silicate as activator\cite{55,61,62}. The blending of three different binders (slag, phyllite dust and silica fume) helped in the effective polycondensation of the ternary blend, which was also supported by the formation of cross-linked C-A-S-H/N-A-S-(H) as observed by NMR spectroscopy (Fig. 9). This explains the outstanding strength and reduced porosity of the

ternary blend, compared to other mixes. The band at 950 to 1000 cm$^{-1}$ represented the formation of C-A-S-H, which was clearly visible in GA and GDA, and it demonstrated that slag played an important role in providing calcium to the system [63–65]. Though the presence of silica in GSA and GDSA mixes helped in the formation of both C-S-H and C-A-S-H, the O-Si-O bending vibrations at 474 cm$^{-1}$ confirmed the presence of unreacted silica in CSA, which was also visible in the FTIR spectrum of silica fume. This supports the hypothesis explained in the NMR findings on the strength properties of the different mixes.

Representative microstructure of these specimens presented microcrack formations (Fig. 14b), which is identified to be the shrinkage cracks due to self-desiccation. Presence of unreacted and partially reacted particles together with the reaction products

Fig. 13. FTIR curve of raw materials and alkali activated blends at 28 d age (Q = 0.30, w/b ratio = 0.30).

Fig. 14. Representative micrographs (2000X magnification) of alkali activated mortar at 28 days of curing age (Q = 0.30, w/b ratio = 0.30).
causes restraints to the shrinkage resulting in microcracks in the gel matrix [66]. Among different mixes, GDA (with phyllite dust) contains many such cracks which can be related to the poor workability (i.e., less water) and low strength to resist the shrinkage (Fig. 6b and Fig. 8b). Low water content in the system worsens the self-desiccation as it causes pore drying due to water consumption for local hydration reactions [67]. This could be a reason for the increase in the open porosity of the GDA mix (Fig. 12). It is also obvious from the micrographs that the ternary blend possessed a uniform matrix that lacked any microcracks (Fig. 14). This finding was consistent with the hypothesis that blended mixes with optimized particle packing helps in the formation of an improved binder matrix that results in increased strength and reduced porosity.

4. Conclusions

This study aimed to develop a high strength one-part alkali-activated mortar by designing mixes using the particle packing optimization technique. In this slag-based mortar, silica fume and phyllite dust were utilized as co-binders to improve the packing of particles of different size ranges, a process which improved the binder matrix of the product.

The experimental results indicated the following:

- The blending of different binders helped in compensating for their negative effects, resulting in an improved mix with enhanced properties. For instance, the negative effect of phyllite dust (GDA) on workability (as low as 20%) was offset by the incorporation of silica fume (GDSA) that maintained the flow (120%).
- Addition of silica fume in the system helped in improving the strength through the formation of cross-linked C-A-S-H and N-A-S-H (Q3 and Q4 silicate species) in the ternary blend. However, the presence of unreacted silica negatively affected the strength of the mix when supplied in excess (GSA).
- In the current one-part AAM, the W/B ratio played an important role in deciding the strength of the mix. Surprisingly, in some cases, the strength increased with increasing W/B ratio. This could be due to the need for a minimum water content to dissolve the sodium silicate and other reactive Si/Al species in one-part AAMs, which are introduced as solids.
- Distribution modulus (Q value) in a particle packing optimization affected each mix differently. Primary mix (GA) with slag gave high strength of 118 MPa with a Q value of 0.25, whereas binary and ternary mixes performed better with a larger Q value of 0.30. Ternary blend (GDSA) with slag, phyllyl dust and silica fume attained the highest compressive strength of 145 MPa.

CRediT authorship contribution statement

Priyadharshini Perumal: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Writing - original draft, Funding acquisition, Project administration. Hari-sankar Sreenivasan: Formal analysis, Investigation, Visualization. Tero Luukkonen: Methodology, Writing - review & editing, Funding acquisition, Project administration. Anu M. Kantola: Formal analysis, Investigation. Ville-Velikko Telikki: Formal analysis, Investigation. Paivo Kinnunen: Conceptualization, Methodology, Supervision, Resources, Funding acquisition, Project administration, Writing - review & editing. Mirja Illikainen: Supervision, Resources, Funding acquisition, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This work was supported by the funding from Business Finland (grant # 1215/31/2015) and Academy of Finland (grant #319676). V.-V.T. thanks Academy of Finland (grants #289649, 294027 and 319216) for the financial support. P.P. gratefully acknowledges the financial support received from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska Curie grant agreement No [839848].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2021.124004.

References

[1] J. Zhang, C. Shi, N. Li, Z. Zhang, N. Farzadnia, Carbon dioxide sequestration by alkali-activated materials, Elsevier Ltd (2018), https://doi.org/10.1016/j.cej.2018.03.138.
[2] A. Heath, K. Paine, M. Manconus, Minimising the global warming potential of clay-based geopolymers, J. Clean. Prod. 78 (2014) 75–83, https://doi.org/10.1016/j.jclepro.2014.04.046.
[3] G. Habert, J.B. d’Espoines de Lacallerie, N. Rossiel, An environmental evaluation of geopolymer based concrete production: Reviewing current research trends, J. Clean. Prod. 19 (11) (2011) 1229–1238, https://doi.org/10.1016/j.jclepro.2011.03.012.
[4] G. Görhan, K. Kürkül, The influence of the NaOH solution on the properties of the fly ash-based geopolymer mortar cured at different temperatures, Compos. Part B Eng. 58 (2014) 371–377, https://doi.org/10.1016/j.compositesb.2013.10.082.
[5] D.M. Roy, Alkali-Activated Cements Opportunities and Challenges, Cem. Concr. Res. 29 (2) (1999) 249–254.
[6] T. Luukkonen, Z. Abdollahnejad, J. Ylimieminen, P. Kittunen, M. Illikainen, One-part alkali-activated materials: A review, Cem. Concr. Res. 103 (2018) 21–34, https://doi.org/10.1016/j.cemconres.2017.10.001.
[7] H. Kühn, Slag cement and process of making the same, US 900 (1908) 939.
[8] J.L. Provis, Alkali-activated materials, Cem. Concr. Res. 114 (2018) 40–48, https://doi.org/10.1016/j.cemconres.2017.02.009.
[9] D.P. Chamliers, P.G. Kidd, P.D. Sleep, Geopolymer cement, US2015032194A1, 2015.
[10] K. Neupane, Fly ash and GGBFS based powder-activated geopolymer binders: A viable sustainable alternative of portland cement in concrete industry, Mech. Mater. 103 (2016) 110–122, https://doi.org/10.1016/j.mechmat.2016.09.012.
[11] K. Neupane, High-Strength Geopolymer Concrete- Properties, Advantages and Challenges, Adv. Mater. 7 (2) (2018) 15, https://doi.org/10.11648/j. am.20180702.11.
[12] C. Li, H. Sun, L. Li, A review: The comparison between alkali-activated slag (Si + Ca) and metakaolin (Si + Al) cements, Cem. Concr. Res. 40 (9) (2010) 1341–1349, https://doi.org/10.1016/j.cemconres.2010.01.020.
[13] A.R. Brough, A. Atkinson, Sodium silicate-based, alkali-activated slag mortars - Part I. Strength, hydration and microstructure, Cem. Concr. Res. 32 (6) (2002) 865–879, https://doi.org/10.1016/S0008-8846(02)00717-7.
[14] and M.B. Palomo, A. M. Grutzeck, Alkali-activated fly ash: a cement for the future, Cem. Concr. Res. 29 (8) (1999) 1323–1329, http://www.sciencedirect.com/science/article/pii/S0008884698000239.
[15] R.J. Myers, S.A. Bernal, J.D. Gehman, J.S.J. Van Deventer, J.L. Provis, L. Struble, The role of Al in cross-linking of alkali-Activated slag cements, J. Am. Ceram. Soc. 98 (3) (2015) 996–1004, https://doi.org/10.1111/jace.13360.
[16] C.K. Yip, G.C. Lukey, J.S.J. Van Deventer, The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation, 35 (2005) 1688–1697, doi:10.1016/j.cemconres.2004.10.042.
[17] B. Nematollahi, J. Sanjayan, F.U.A. Shaikh, Synthesis of heat and ambient cured one-part geopolymer mixes with different grades of sodium silicate, Ceram. Int. 41 (4) (2015) 5696–5704, https://doi.org/10.1016/j.ceramint.2014.12.154.
[18] L. Coppola, D. Coffetti, E. Crotti, Pre-packed alkali activated cement-free mortars for repair of existing masonry buildings and concrete structures, Constr. Build. Mater. 173 (2018) 111–117, https://doi.org/10.1016/j.conbuildmat.2018.04.034.
