Feasibility Study of Metakaolin-Based Geopolymer as Binder for Construction Mortar

Oscar D. Huang[1]; Nathaniel J. Lies[2]; and Miladin Radovic, Ph.D.[3]

[1]Dept. of Materials Science and Engineering, Texas A&M Univ., TX. E-mail: ohuang2@tamu.edu
[2]Dept. of Materials Science and Engineering, Texas A&M Univ., TX. E-mail: liesmp@tamu.edu
[3]Dept. of Materials Science and Engineering, Texas A&M Univ., TX. E-mail: mradovic@tamu.edu

ABSTRACT

Geopolymer is an aluminosilicate network polymer that has gained interest in recent years as an eco-friendly alterative to ordinary Portland cement for transportation infrastructure. This novel material can be processed from waste and/or widely available natural materials under ambient conditions. In this study, a comprehensive set of metakaolin-based geopolymers and geopolymer mortars with construction sand were processed using different SiO_2/Al_2O_3 ratios and water/solid ratios for geopolymer binder and cured at ambient conditions for 14 days. Pure geopolymer and geopolymer mortar samples were tested for compressive strength, density, and open porosity. The results show that the composition of geopolymers strongly affects their properties especially their compressive strength. Samples with various compositions were characterized with scanning electron microscopy (SEM) to examine the morphological and structural effect from the compositional parameters.

INTRODUCTION

Ordinary Portland cement (OPC) is indisputably one of the most used materials in transportation infrastructures since it is the widely used in concrete structures such as pavements, bridges, etc. However, the production of OPC requires heating the raw materials (i.e. clay and lime) to high temperatures of around 1350ºC (Gartner 2004). Gartner estimated that the production of 1 ton of OPC produces roughly 1 ton of CO_2 from the energy consumption to achieve the high temperature as well as the chemical reaction between the raw materials (Gartner 2004). In 2015, it was estimated that 3.5 billion tons of OPC was produced worldwide, which roughly equates to 5% of total global anthropogenic CO_2 emission (Gartner 2004; Shayan 2016).

One of the environmentally friendly alternatives that many researchers have recently started to focus on is geopolymer-based binders. Davidovits developed and coined the term "geopolymers" (GP) in the 1970s (Davidovits 1991; Davidovits 2017) to refer to the class of inorganic alumio-silcate polymers with amorphous structure. GPs can be processed at near ambient conditions (typically below 100ºC) to have high compressive strength, low shrinkage, and performance similar to that of traditional cementitious materials. Additionally, GPs have several advantages over OPC, these include producing significantly less greenhouse gas emissions during production, good acid and fire resistance, and lower thermal conductivity (Duxson et al. 2007; Gartner 2004). Chemically, GPs are alkali aluminosilicates with the empirical formula, $M_n[-(SiO_2)_z - AlO_2-]_n \cdot wH_2O$ where M is the alkali metal cation, n is the degree of polymerization, z is the Si/Al ratio, and w is the molar water quantity. It is worth noting here, that the activating metal cation M (usually Na^+, K^+, Cs^+, etc.) is believed to stay in the geopolymer framework cavities close to Al and balance the negative charge of the IV-coordinated $[-AlO_2-]^-$ (Van Jaarsveld et al. 1999). In the past 50 years, GPs have been applied to numerous applications ranging from things such as concrete structure, soil stabilization, fire-proof coating, thermal insulations, and waste containment, to many other novel applications (Ahmari and Zhang 2013; Cheng et al. 2012; Davidovits 2005; Kan et al. 2020; Papa et al. 2019; Provis and Van Deventer 2009; Tennakoon et al. 2017).

Table 1. The list of GP compositions tested in this study.

List of GP Compositions	
Na241	K231
Na251	K241
Na(2.5)31	K(2.5)21
Na(2.5)41	K(2.5)31
Na321	K321
Na331	K331
Na421	K421
Na431	K431

BACKGROUND

The synthesis of GP requires an aluminosilicate rich source, alkali hydroxide (e.g. NaOH, KOH), and a source of additional silica (e.g. silica fume, sodium silicate). Arguably, one of the most important components of GP is the aluminosilicate rich source as there are a number of possibilities, including clays (e.g. metakaolin), industrial waste (e.g. fly ash, steel slag), and some locally available resources (e.g. volcanic ash, rice husk) (Mehta and Siddique 2016; Shayan 2016; Van Jaarsveld et al. 2004; Xu and Van Deventer 2000). All of these are feasible candidates for geopolymerization because they have a significant amount of amorphous phases containing Al and Si that are highly reactive, which allows the highly alkali aqueous solutions to dissolve and dissociate the aluminosilicate source to produce monomeric and/or oligomeric species of Al and Si, which subsequently from –Al-O-Si- or –Si-O-Si- chains during a polycondensation process that releases excess water. Those chains continue to grow and crosslink during the polycondensation process until an amorphous gel with a complex 3D structure is formed. The GPs continue to polycondensate and lose water until they are fully cured. This curing process takes approximately 21 days at room temperature (Perera et al. 2007). The final GP structure can be described as an amorphous, 3-D framework of corner-sharing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra in IV-fold coordination (Duxson et al. 2005). The IV-coordinated aluminum present in the structure differentiates a GP from other poly-aluminosilicate materials which typically have VI-coordinated aluminum. The negatively charged $[AlO_4]^{5-}$ tetrahedra in IV-fold coordination are balanced by residual alkali cations which remain loosely incorporated into the GP structure. These cations are hydrophilic and retain some water within pores in the GP structure after curing (Lizcano et al. 2012; Phair and Van Deventer

2001).

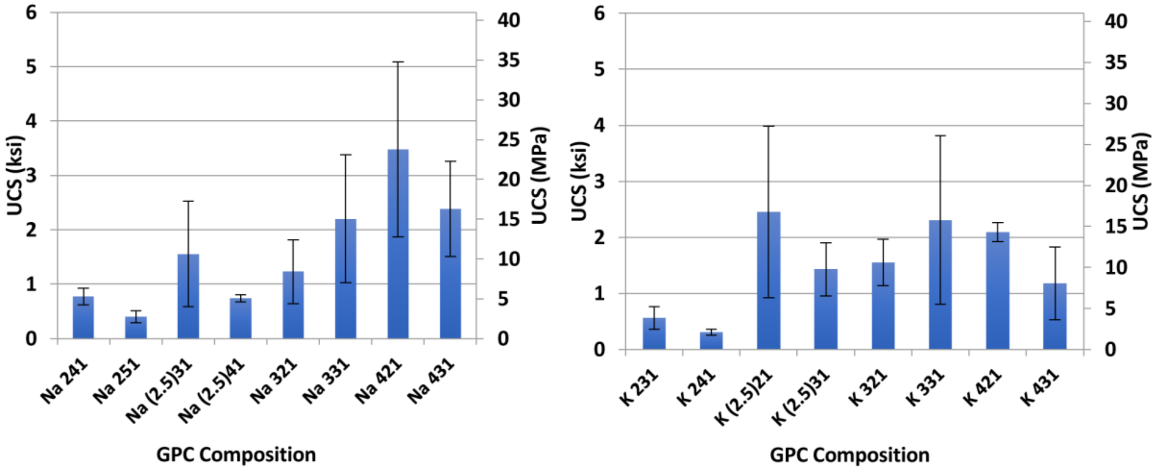

Figure 1. Average ultimate compressive strength (UCS) of (a) pure Na-based GPs and (b) K-based GPs after a 14-day curing. Error bars represent standard deviation from 5 measurements.

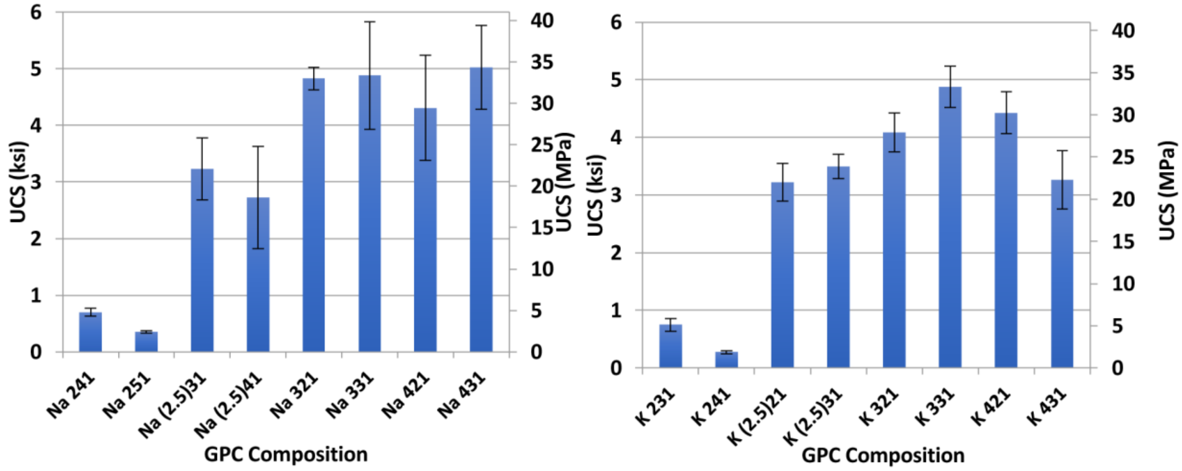

Figure 2. Average ultimate compressive strength (UCS) of (a) Na-based GP mortars and (b) K-based GP mortars after a 14-day curing. Error bars represent standard deviation from 5 measurements.

As GP is a complex materials system, many factors influence its formation and properties. Several important considerations are the aluminosilicate source, the SiO_2/Al_2O_3 ratio in precursor materials, the water to solid ratio used during synthesis, the type and amount of alkali activator, and mixing and curing conditions. The influence of all these factors on structure and properties of GPs has been extensively studied over the last few decades and is summarized elsewhere (Davidovits 2005; Duxson et al. 2007; Provis and Van Deventer 2009; Shayan 2016). For example, it is well established by now that higher SiO_2/Al_2O_3 ratio allows for a more complex interlinking in the GP framework during polycondensation. This leads to overall enhancement in properties such as higher mechanical strength (Lizcano et al. 2012; Phair and Van Deventer 2001; Xu and Van Deventer 2002). Another critical factor during polycondensation is the availability of Al in the GP gel, as its release rate directly affects many GP properties, including strength, microstructure, acid resistance, the curing profile, and the strength development profile (Fernández-Jiménez et al. 2006; Weng et al. 2005; Xu and Van Deventer 2003). While the Al in metakaolin-based GPs is readily available due to the significant portion of Al in the meta-stable V-coordination structure (Duxson et al. 2005), the Al in fly ash and other industrial waste-based GPs are much more slowly released and that could lead to incomplete geopolymerization and/or to slower curing times (Rees et al. 2008). High water content used during synthesis was also found to affect structure and properties. Excess water occupies volume and then evaporates from the geopolymer leaving a lower density solid with a more open GP framework (Lizcano et al. 2012). An increase in the alkali/Al ratio has been theorized to act as a “chain terminator” during polycondensation and prevent the geopolymer chains from fully developing. In addition, the extra alkaline content makes the GP more hydrophilic and leads to an increase in the residual chemically bonded interstitial water after curing and water absorption (Lizcano et al. 2012; Provis and Van Deventer 2009). This study investigates the effect of composition on the properties of pure GP and GP mortar.

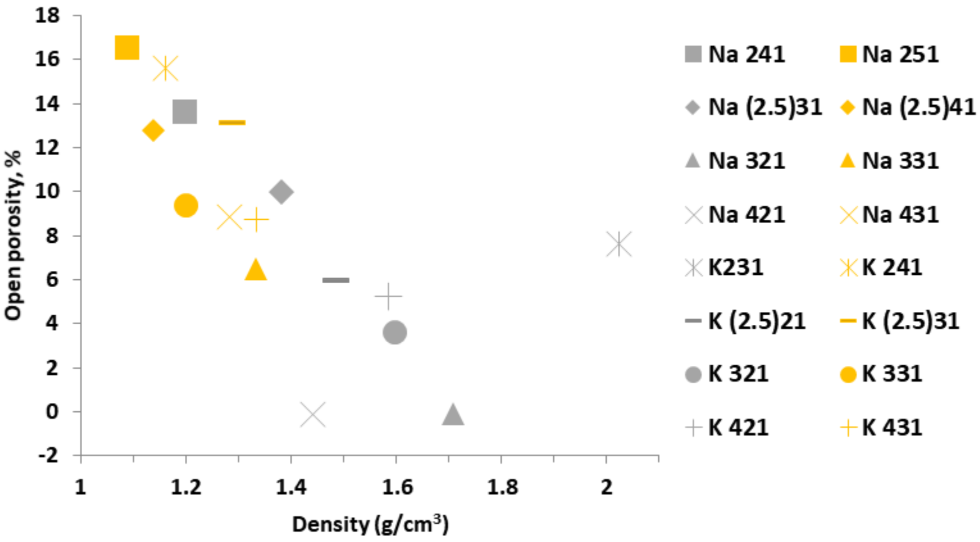

Figure 3. Open porosity vs. Density plot of pure GP samples after a 14-day curing.

METHODOLOGY

The GPs used in this study were synthesized using either sodium or potassium hydroxide (Noah Technology, TX), amorphous fumed silicon (IV) oxide (Alfa Aesar, MA) with 350- 410 m^2/g specific surface area, MetaMax® (BASF Catalysts LLC, NJ) metakaolin, and deionized water. Metakaolin (MK) was chosen as the aluminosilicate source since it is a relatively pure source of aluminosilicate (with SiO_2/Al_2O_3 ratio equal to 2.05) making it a more ideal GP precursor for the purpose of this research than the more commonly used fly ash which has higher impurities.

The framework for development of GPs in this study is based on the previous work (Lizcano et al. 2012). The 16 different GP compositions are chosen to investigate the effect of cation (Na vs. K), SiO_2/Al_2O_3 ratio (2-4), and the water/solids ratio. The complete list of compositions can be found in Table 1. Note that all GP samples with different compositions are labeled as KXYZ or NaXYZ, where the first letters denote potassium (K) or sodium (Na) while XYZ numbers denote SiO_2/Al_2O_3 ratio, water to solid ratio used to prepare GP, and Na/Al or K/Al ratio respectively. For example, GP sample K421 is sample prepared with K-activator, and $SiO_2/Al_2O_3=4$, water/solid ratio=2, and K/Al=1.

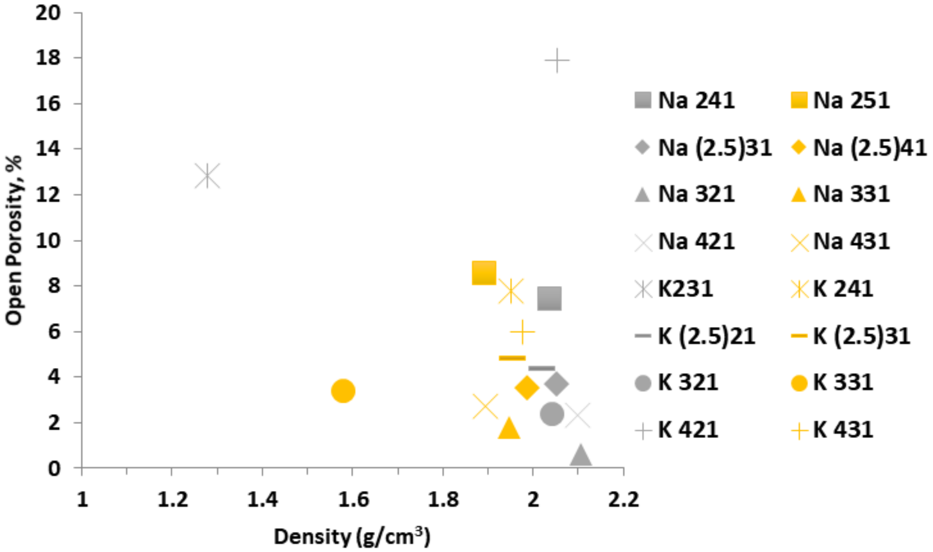

Figure 4. Open porosity vs. Density plot of GP mortar samples after a 14-day curing.

The sodium or potassium hydroxide was first dissolved in deionized water to create a highly alkaline solution. The amorphous fumed silicon oxide was then added to adjust the SiO_2/Al_2O_3 ratio of the final product and create the activating solution for the synthesis of GP. The activating solution was then mixed with MK, in a high-shear mixer for 6 minutes at 400 revolutions per minute (RPM) to create a homogenous mixture, referred to as GP paste. For the GP mortar samples, pure GP paste was manually mixed with masonry sand at a GP to dry sand weight ratio of 1:2.75 (27wt.% of GP binder in the mortar), which is the same as the OPC to dry sand ratio that is required for standard OPC mortars according ASTM C109 (ASTM 2016). As a part of ASTM C109, the mortar samples were made with sand that has particle size distribution that follows ASTM C778 (ASTM 2017). Both GP paste and GP mortars were cast in cylindrical molds with the dimensions of 2.54 cm (1 in.) in both height and diameter. They were then cured for seven days in a sealed container under ambient conditions before removing the samples from the molds for additional curing of seven days under open ambient conditions before testing. The density and open porosity of the samples were measured using Archimedes' method according to ASTM C830-00 (ASTM 2016). Density and open porosity were calculated using following equations:

$$\rho = \frac{m_{dry} * \rho_{ethanol}}{m_{wet} - m_{suspended} + m_{wire}} \qquad [1]$$

$$P_{open} = \frac{m_{wet} - m_{dry}}{m_{wet} - m_{suspended} + m_{wire}} * 100\% \qquad [2]$$

where ρ is measured density (g/cm³), m_{dry} is dry mass (g), $\rho_{ethanol}$ is density of ethanol (g/cm³), m_{wet} is mass of sample with ethanol occupying the open pores (g), $m_{suspended}$ is mass of sample while suspended in ethanol (g), m_{wire} is mass of the part of Archimedes' set up that's used to suspend sample in ethanol (g), and P_{open} is open porosity (%). To measure m_{wet}, the samples were submerged in 200 proof ethanol, and placed into a vacuumed desiccator for 20 minutes. The samples were then removed, and the surface was quickly dried with a cloth towel to remove excess ethanol before measuring m_{wet}. The samples were then left in ambient condition for a day so the ethanol would evaporate. After which, they were tested for their Ultimate Compressive Strength (UCS) with an 810 Materials Testing System (MTS System Corporation, MN) in compression mode with constant displacement rate of 0.60 mm/min.

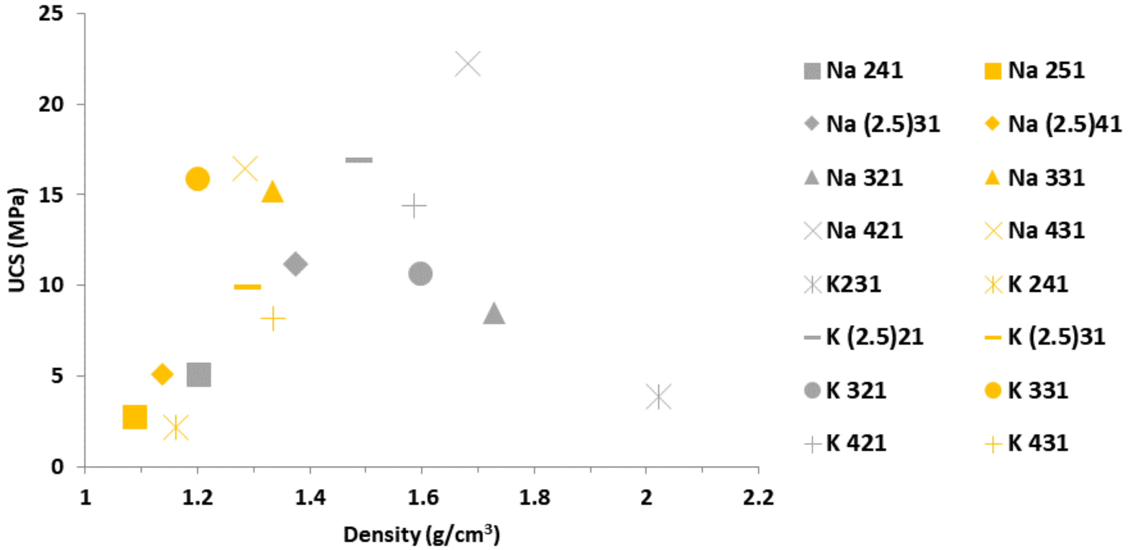

Figure 5. Average Ultimate Compressive Strength (UCS) vs. Density plot of Pure GPs after a 14-day curing.

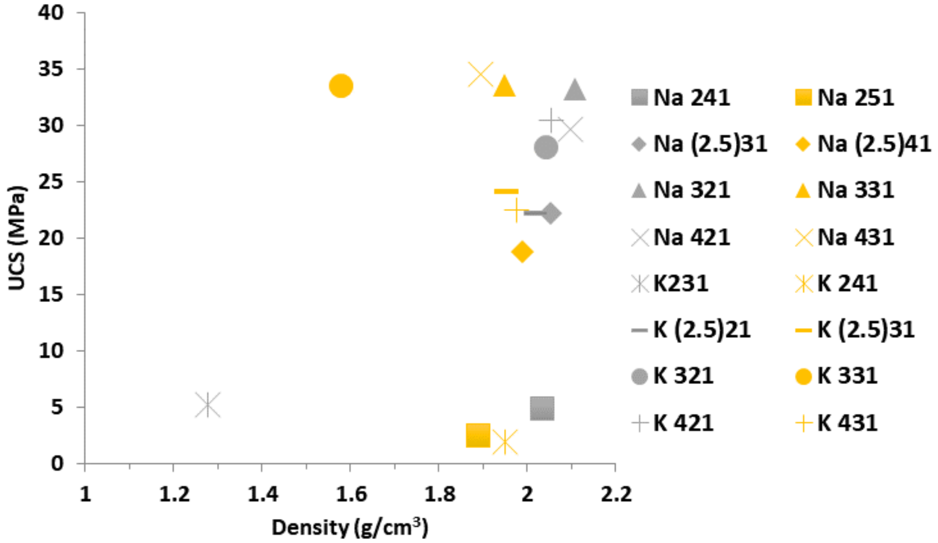

Figure 6. Average Ultimate Compressive Strength (UCS) vs. Density plot of GPs mortars after a 14-day curing.

After the comprehensive parametric studies, one of the best performing, and one of the worst performing compositions in terms of UCS were characterized with scanning electron microscopy (SEM) to gain some insight behind the differences in properties. SEM analyses of all samples were conducted with the JEOL JSM-7500F (JEOL USA Inc, MA) FE-SEM to study the microstructure of the samples under back-scattered imaging.

RESULTS AND DISCUSSION

The results of UCS tests for both pure GPs and GP mortars are shown in Figures 1-2. Figure 1a shows that, in general, the compressive strength of Na-based pure GP increases with increasing SiO_2/Al_2O_3 ratio and deceasing H_2O/Solids ratio, which is in good agreement with previously published results for GPs cured at elevated temperatures (Duxson et al. 2007; Lizcano et al. 2012). The only exception is Na321 which can be explained by the H_2O/Solids ratio not allowing for proper mixing. Therefore, its unexpectedly low strength is most likely due to an excessive amount of unreacted MK and air pores within the samples. On the other hand, Figure 1b shows that K-based pure GPs do not seem to follow the expected trend with respect to SiO_2/Al_2O_3 ratio as the Na-based pure GPs did. As it can be seen in Figure 1, K(2.5)21 and K331 have the highest strengths, while the strength of K421 is close and to that of K(2.5)21, although it contains a higher SiO_2/Al_2O_3 ratio and the same H_2O/Solids ratio. Even though the K-based pure GPs do not exhibit the expected trend of UCS with SiO_2/Al_2O_3 ratio, in general, it does follow the trend of decreasing UCS with increased H_2O/Solids ratio. The lack of clarity in trends for K-based pure GPs is most likely due to the fact that K-based GPs tend to have lower reaction kinetics, therefore, it's likely that a 14-day ambient curing period isn't long enough to fully complete geopolymerization rection. Therefore, a longer curing period will be needed for a proper comprehensive study of K-based GP. Additional evidence for this claim can be found in the fact that K-based GPs show, in general, lower UCS when compared to Na-based Geopolymers with the same SiO_2/Al_2O_3 and H_2O/Solids ratios.

Looking at the UCS results of the GP mortar specimens in Figure 2, the addition of sand seems to increase the UCS and decrease the variability for most of the compositions. The increase in strength is in direct contrast to what has been observed in the case of OPC mortars, where addition of sand to OPC significantly lowers the strength (Toutanji and El-Korchi 1995; Zhao et al. 2014). However, neither Na-based nor K-based GP mortar seem to follow the same trends as pure GPs in regard to SiO_2/Al_2O_3 and H_2O/Solids ratios used for GP binder preparation. It seems that for Na-based GP mortars prepared with $SiO_2/Al_2O_3 \geq 3$, UCS is independent of the GP binder composition, while for K-based GP mortars the one with intermediate SiO_2/Al_2O_3 and H_2O/Solids ratios, namely K331, shows the highest compressive strength.

Results of open porosity and density measurements in Figures 3 and 4 shows that both pure GPs and GP mortar specimens exhibit an expected decrease in open porosity with increasing density, with a few exceptions such as pure K231 GP and K331 and K321 GP mortars. On the other hand, the UCS vs. Density plot for pure GPs shown in Figure 5 shows a much more interesting trend between the two properties. It suggests that optimal density for pure GP is ~1.6 g/cm^3, despite the conventional assumption that less open GP network structures with higher density should yield higher strength. Note that the two compositions with the highest density, namely Na321 and K231, were very thick and lacked workability, and therefore they contained large pores of entrapped air. Unlike in the case of pure GP, UCS of the GP mortar samples does not seem to depend strongly on the density of the samples. This can be seen in Figure 6 and is most likely because the mortar specimens were made with large amount of sand (a mortar sample is 27 wt% binder), which means the variation in the density of the in binder would not contribute significantly to the overall density of the mortar samples.

Based on the results shown above, the GP mortars prepared with Na431 and K231 GP binders show one of the highest and lowest UCSs, respectively. SEM imaging of those two samples in Figure 7 clearly shows different morphology of GP binder in Na431 and K231 mortar samples. This suggests that the degree of reaction of MK in GP binder is crucial for strength of the mortar samples. This can be qualitatively determined through the larger amount of observable unreacted MK particles in the K231 GP binder (Figures 7a and b) when compared to the Na431 GP binder in Figures 7c and d. In addition, although Na431 GP binder contains some larger cracks, it seems to adhere much better to the sand particles, as compared to the K231 binder. The better adhesion to sand particles also can contribute the higher compressive strength observed in those samples.

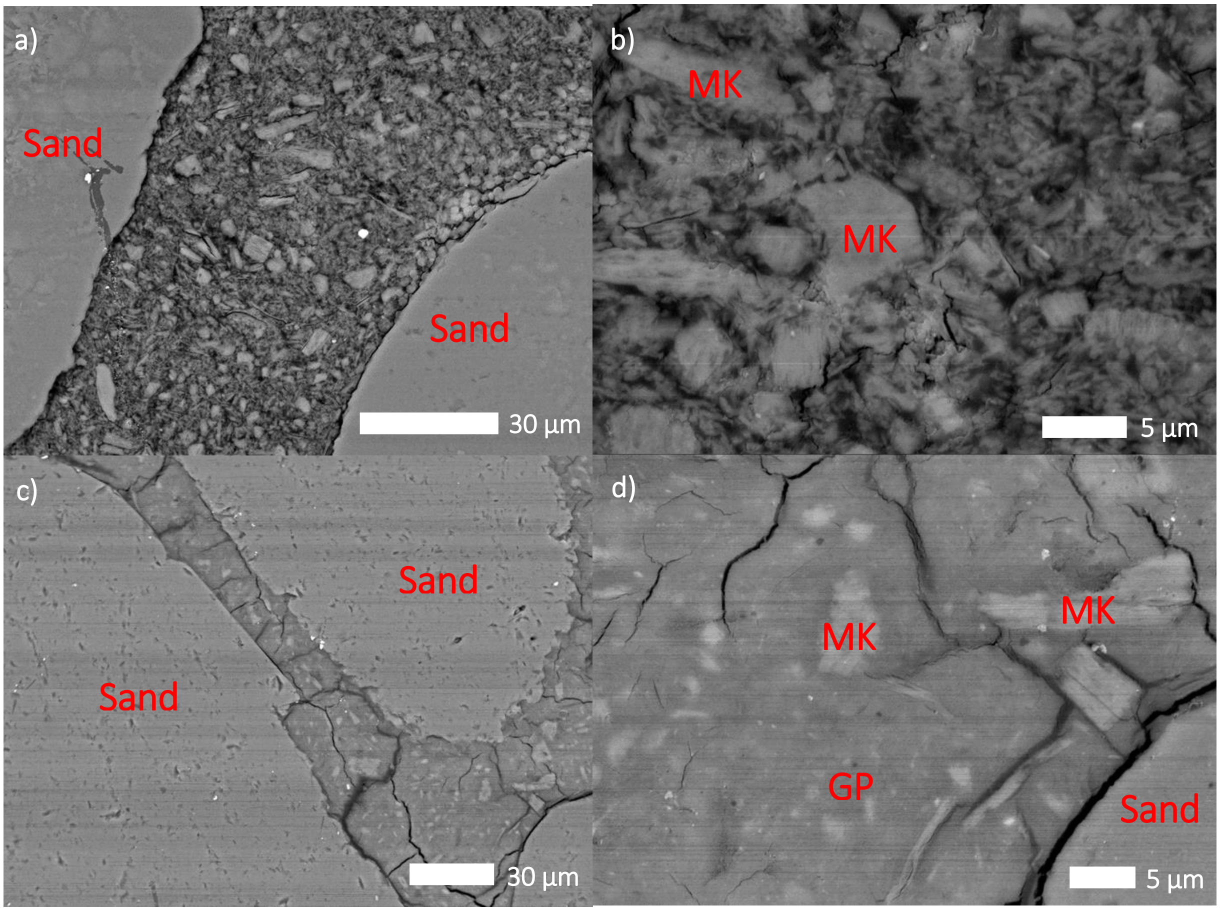

Figure 7. Back-Scattered Electron SEM micrograph of a) K231 mortar at low magnification, b) K231 mortar at high magnification, c) Na431 mortar at low magnification, and d) Na431 mortar at high magnification

CONCLUSION AND FUTURE WORK

Overall, GP-based binders demonstrated promising potential for use in mortars after 14-day curing in ambient conditions. The study showed that the chemical composition (i.e. SiO_2/Al_2O_3 ratio) has a significant effect on the UCS of GP binders. In that regard, the results of this study seem to agree with previous studies carried out on GP samples cured at elevated temperatures: that higher SiO_2/Al_2O_3 ratio yields higher UCS (Duxson et al. 2007; Lizcano et al. 2012). The addition of sand into GPs also seem to improve their strength significantly. Results of this study also show that strength of the GP mortars with 27 wt% binder that were cured in ambient conditions also depends, not only on the composition of the binder, but also on the extent of the geopolymerization of the binder as the samples with larger amounts of unreacted MK in the GP binder show significantly lower strengths.

REFERENCES

Ahmari, S., and Zhang, L. (2013). "Durability and leaching behavior of mine tailings-based geopolymer bricks." *Construction and Building Materials*, 44, 743-750.

ASTM (2016). "Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)." ASTM International, West Conshohocken, PA.

ASTM (2016). "Standard Test Methods for Apparent Porosity, Liquid Absorption, Apparent Specific Gravity, and Bulk Density of Refractory Shapes by Vacuum Pressure." ASTM International, West Conshohocken, PA.

ASTM (2017). "Standard Specification for Standard Sand." ASTM International, West Conshohocken, PA.

Cheng, T. W., Lee, M. L., Ko, M. S., Ueng, T. H., and Yang, S. F. (2012). "The heavy metal adsorption characteristics on metakaolin-based geopolymer." *Applied Clay Science*, 56, 90-96.

Davidovits, J. (1991). "Geopolymers: inorganic polymeric new materials." *Journal of Thermal Analysis Calorimetry*, 37(8), 1633-1656.

Davidovits, J. (2005). *Geopolymer, green chemistry and sustainable development solutions: proceedings of the world congress geopolymer 2005*, Geopolymer Institute.

Davidovits, J. (2017). "Geopolymers: Ceramic-like inorganic polymers." *J. Ceram. Sci. Technol*, 8(3), 335-350.

Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., and Van Deventer, J. S. J. (2007). "Geopolymer technology: The current state of the art." *Journal of Materials Science*, 42, 2917-2933.

Duxson, P., Mallicoat, S. W., Lukey, G. C., Kriven, W. M., and van Deventer, J. S. (2007). "The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 292(1), 8-20.

Duxson, P., Provis, J. L., Lukey, G. C., Mallicoat, S. W., Kriven, W. M., and Van Deventer, J. S. J. (2005). "Understanding the relationship between geopolymer composition, microstructure and mechanical properties." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 269, 47-58.

Duxson, P., Provis, J. L., Lukey, G. C., Separovic, F., and van Deventer, J. S. (2005). "29Si NMR study of structural ordering in aluminosilicate geopolymer gels." *Langmuir*, 21(7), 3028-3036.

Fernández-Jiménez, A., Palomo, A., Sobrados, I., and Sanz, J. (2006). "The role played by the reactive alumina content in the alkaline activation of fly ashes." *Microporous Mesoporous Materials*, 91(1-3), 111-119.

Gartner, E. (2004). "Industrially interesting approaches to "low-CO2" cements." *Cement and Concrete research*, 34(9), 1489-1498.

Kan, L.-l., Wang, W.-s., Liu, W.-d., and Wu, M. (2020). "Development and Characterization of Fly Ash Based PVA Fiber Reinforced Engineered Geopolymer Composites Incorporating Metakaolin." *Cement and Concrete Composites*, 103521.

Lizcano, M., Gonzalez, A., Basu, S., Lozano, K., and Radovic, M. (2012). "Effects of water content and chemical composition on structural properties of alkaline activated metakaolin-based geopolymers." *Journal of the American Ceramic Society*, 2169-2177.

Lizcano, M., Kim, H. S., Basu, S., and Radovic, M. (2012). "Mechanical properties of sodium and potassium activated metakaolin-based geopolymers." *Journal of Materials Science*, 47, 2607-2616.

Mehta, A., and Siddique, R. (2016). "An overview of geopolymers derived from industrial by-products." *Construction and Building Materials*, 127, 183-198.

Papa, E., Medri, V., Paillard, C., Contri, B., Murri, A. N., Vaccari, A., and Landi, E. (2019). "Geopolymer-hydrotalcite composites for CO2 capture." *Journal of Cleaner Production*, 117738.

Perera, D., Uchida, O., Vance, E., and Finnie, K. J. J. o. m. s. (2007). "Influence of curing schedule on the integrity of geopolymers." *Journal of Materials Science*, 42(9), 3099-3106.

Phair, J., and Van Deventer, J. (2001). "Effect of silicate activator pH on the leaching and material characteristics of waste-based inorganic polymers." *Minerals Engineering*, 14(3), 289-304.

Provis, J. L., and Van Deventer, J. S. J. (2009). *Geopolymers: structures, processing, properties and industrial applications*, Elsevier.

Rees, C. A., Provis, J. L., Lukey, G. C., Van Deventer, J. S. J. C., Physicochemical, S. A., and Aspects, E. (2008). "The mechanism of geopolymer gel formation investigated through seeded nucleation." *Colloids Surfaces A: Physicochemical Enginering Aspects*, 318(1-3), 97-105.

Shayan, A. (2016). "Specification and use of geopolymer concrete in the manufacture of structural and non-structural components: review of literature."

Tennakoon, C., Shayan, A., Sanjayan, J. G., and Xu, A. (2017). "Chloride ingress and steel corrosion in geopolymer concrete based on long term tests." *Materials & Design*, 116, 287-299.

Toutanji, H. A., and El-Korchi, T. (1995). "The influence of silica fume on the compressive strength of cement paste and mortar." *Cement and Concrete Research*, 25(7), 1591-1602.

Van Jaarsveld, J., Van Deventer, J., and Lukey, G. (2004). "A comparative study of kaolinite versus metakaolinite in fly ash based geopolymers containing immobilized metals." *Chemical Engineering Communications*, 191(4), 531-549.

Van Jaarsveld, J., Van Deventer, J., and Schwartzman, A. (1999). "The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics." *Mineral Engineering*, 12(1), 75-91.

Weng, L., Sagoe-Crentsil, K., Brown, T., Song, S. J. M. S., and B, E. (2005). "Effects of aluminates on the formation of geopolymers." *Materials Science Engineering: B*, 117(2), 163-168.

Xu, H., and Van Deventer, J. (2000). "The geopolymerisation of alumino-silicate minerals." *International Journal of Mineral Processing*, 59(3), 247-266.

Xu, H., and Van Deventer, J. S. (2002). "Geopolymerisation of multiple minerals." *Minerals Engineering*, 15(12), 1131-1139.

Xu, H., and Van Deventer, J. S. (2003). "Effect of source materials on geopolymerization." *Industrial & Engineering Chemistry Research*, 42(8), 1698-1706.

Zhao, H., Xiao, Q., Huang, D., and Zhang, S. (2014). "Influence of pore structure on compressive strength of cement mortar." *The Scientific World Journal*, 2014.