COMPLETE RECYCLING AND UTILIZATION OF WASTE CONCRETE THROUGH GEOPOLYMERIZATION

by

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DEDICATION

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ABSTRACT

This research investigates complete recycling and utilization of waste concrete to produce new structural concrete through geopolymerization. The investigation was conducted through both macro- and micro/nano-scale studies. First the geopolymer paste synthesized using a mixture of waste concrete fines (WCF) and class F fly ash (FA) as the source material and a mixture of NaOH solution (N) and Na2SiO3 solution (SS) as the alkaline activating agent was studied. Various NaOH concentrations, SS/N ratios, and WCF contents were used to produce geopolymer paste specimens in order to study their effect on the properties of the geopolymer paste. Uniaxial compression tests were conducted to measure the strength of the geopolymer paste specimens. X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), and Fourier transform infrared spectroscopy (FTIR) analyses were performed to investigate the micro/nano-structure, morphology and phase/surface elemental compositions of the geopolymer paste and the effect of calcium (Ca) on them. The results indicate that by using 10 M NaOH solution, SS/N of 2 and 50% WCF, the highest geopolymer paste strength can be obtained.

Second, the interfacial transition zones (ITZs) between geopolymer (GP) and recycled aggregates (RA) were studied. Considering that RA consist of the stone particles and the attached paste/mortar from the original ordinary Portland cement (OPC) concrete, both the ITZs between GP and natural aggregate (NA) and those between GP and residual OPC paste/mortar (ROPM) were studied. For comparison, the ITZs between OPC paste and NA and those between OPC paste and ROPM were also investigated. 4-point bending tests were conducted to measure the bonding strength of the different types of ITZs at water to solid (W/S) ratio of 0.30, 0.35 and 0.40 for the geopolymer and OPC pastes after 7 and 14 days curing, respectively. SEM imaging was performed to investigate
the microstructure of the ITZs. The results indicate that when NA is used, the bonding strength of both the GP-NA and OPC-NA ITZs decreases with higher water to solid (W/S) ratio. When ROPM is used, higher W/S ratio leads to smaller bonding strength for the GP-ROPM ITZ but greater bonding strength for the OPC-ROPM ITZ. Based on the measured bonding strength values for NA- and ROPM-based ITZs, the bonding strength of the GP-RA and OPC-RA ITZs was estimated by considering the average area coverage of ROPM on the RA surface. The GP-RA ITZ has the highest bonding strength among the different ITZs, implying the great potential for utilizing waste concrete (both the WCF and the RA) to produce geopolymer concrete.

Third, based on the studies on geopolymer paste and ITZs, geopolymer concrete (GPC) was produced and studied using WCF and FA as the cementitious material and RA as the aggregate. For comparison, GPC using NA was also produced and studied at similar conditions. Various NaOH concentrations, SS/N ratios, and cement (WCF and FA) to aggregate (C/A) ratios were used to produce GPC specimens in order to study their effect on the behavior of GPC. The effect of water content and curing temperature on the initial setting time and 7-day unconfined compressive strength (UCS) of the GPC was also studied. The results show that the GPC produced from RA has higher UCS than the GPC from NA at both room curing temperature and 35 ℃ curing temperature. Based on this study, it can be concluded that waste concrete can be completely recycled and used to produce new structural concrete based on the geopolymerization technology.

Fourth, considering that the Si/Al and Na/Al ratios have great effect on the geopolymerization process and the properties of the final geopolymer product, a study was conducted on copper mine tailings (MT)-based geopolymer containing different amount of aluminum sludge (AS). The results indicate that by including AS and utilizing appropriate amount of NaOH, the UCS can be increased significantly. The main reason is because the addition of AS along with utilization of
appropriate amount of NaOH makes both the Si/Al and Na/Al ratios reach the optimum values for geopolymerization, leading to higher degree of geopolymerization and more compact geopolymer microstructure. It is noted that although this study is not directly on waste concrete, it provides useful information for optimizing the design on complete recycling and utilization of waste concrete to produce new GPC.

Finally, to better understand the effect of Ca on the geopolymerization process and the properties of geopolymer, molecular dynamics (MD) simulations were performed on geopolymer at different Ca contents. The molecular models at different Ca contents were constructed and uniaxial compression test was then performed on the numerical specimens. The results indicate that MD simulation is an effective tool for studying the effect of Ca on the properties of geopolymer at nano-scale.
CHAPTER 1

INTRODUCTION

1.1 Background

The American Society of Civil Engineers (ASCE) gave the infrastructure in the U.S. an overall grade of “D+” in the latest 2013 Report Card for American’s Infrastructure [1]. This grade reflects that the nation’s infrastructures are in a critical situation and need to be repaired and upgraded. Repairing and upgrading these infrastructures will require a huge amount of new construction materials, presenting the whole civil engineering industry a great challenge.

Concrete is widely used in the construction and repair of infrastructures. Ordinary Portland cement (OPC) is commonly used as the binder material for concrete. Production of OPC consumes a large amount of natural materials and releases a substantial quantity of greenhouse gases. Generally, the process of producing 1 ton of OPC requires 1.5 tons of resource materials and releases 0.9 ton of CO2 into the atmosphere [2, 3]. Beside the cement, production of concrete also requires sand and aggregates. The process of producing the sand and aggregates is also energy intensive and creates a significant amount of wastes as well. Further, the shortage of sand and aggregates in many parts of the U.S. leads to long-distance hauling and higher costs [4]. Growing awareness of sustainability and global warming issues in recent decades has been pushing the whole construction industry to seek alternative materials [5-7].

On the other hand, the process of repairing and upgrading the deteriorating infrastructures generates a tremendous amount of waste concrete. It is increasingly difficult to find suitable locations for disposing of the waste concrete. In order to address this issue, different agencies and
institutions have started to look for new methods for recycling waste concrete. Although much research has been done, so far the recycling of waste concrete is still predominately limited to the utilization of concrete aggregates in low-specification applications such as base course and non-structure filling [8-10]. Generally, the waste concrete crushing process generates both aggregates (coarse and fine) and fines. The concrete aggregate (called recycled aggregate – RA later) contains both the original stone particles and the cement paste/mortar from the original concrete remains attached to them. The low quality of the RA is mainly due to the attached paste/mortar. Compared to natural aggregates (NA), RA has higher water absorption, abrasion loss, crushability and quantity of dust particles, but lower bulk density and specific gravity. The low quality of RA generally leads to the new OPC concrete containing RA with inferior strength, durability and shrinkage properties. Therefore, the utilization of RA in the production of new structural concrete is limited.

Researchers have investigated the utilization of RA to partially replace NA in the production of new OPC concrete. Tam et al. [11] studied the properties of new OPC concrete by using different amounts of RA and recommended a limit of 30% RA. They [12] continued the study by developing a two-stage mixing method to improve the strength of OPC concrete containing RA. The results show that by using the two-stage mixing method, the strength of new OPC concrete containing 20% RA can be improved by 21%. Based on the study, they recommended that 25% to 40% of RA could be used in the production of new OPC concrete. González-Fonteboa et al. [13] tried to pre-wet RA for 10 minutes before the concrete mixing in order to keep the consistency. By doing so, they concluded that when 20% of coarse NA is replaced by RA, the stress–volumetric strain curves and the critical stress values of the new OPC concrete are similar to those of the OPC concrete containing 100% NA.
Researchers have also developed aggregate refining methods to improve the quality of RA by removing the attached paste/mortar, including “heating and rubbing” [14], “mechanical grinding” [15] and “microwave heating” [3]. However, these methods are energy intensive and produce additional fines which need to be disposed of [16]. Obviously, an ideal solution is complete recycling and utilization of waste concrete (both RA and fines) in the production of new structural concrete.

Very few researchers have investigated complete recycling of waste concrete. Tomosawa and Noguchi [17] combined OPC, crushed limestone and limestone dust to produce 100% recyclable concrete. Since limestone is the only filler in the concrete, the concrete can be crushed and then calcined at very high temperature. The resulting clinker was then added with a suitable amount of gypsum and milled to produce recycled cement. Costes et al. [18] also did research on complete recycling of waste concrete. They concluded that the pure hydrated cement can be re-clinkered through the normal kiln process at 1,450 °C. So a method for separating cement, sand and aggregates was developed. By heating the crushed waste concrete to 700 °C, the adherence of hydrated cement to sand and aggregates was weakened. Then a ball milling machine was applied to separate the hydrated cement from sand and aggregates. The separated hydrated cement along with an additive if necessary, was then re-clinkered to produce new cement. It can be seen that both methods consume a significant amount of energy and thus generate a tremendous amount of greenhouse gases. Therefore, to completely recycle waste concrete eco-friendly, a method which does not require the re-clinkering process at high temperature should be developed [7].

In recent years, a new technology called geopolymerization shows that it has advantages in reusing various types of wastes to produce new construction materials. Geopolymer is a product from the reaction of solid aluminosilicates with a high concentration alkaline hydroxide and/or silicate
solution. Compared to OPC, geopolymer products have several advantages. For example, the aluminosilicate materials can be from different sources and most of them are industry wastes. Production of geopolymer products from wastes not only supplies new construction materials but also addresses the issues such as disposal of industry wastes. Unlike the OPC which requires high temperature clinkering for its production, geopolymer can be produced at an ambient or slightly elevated temperature. It is also noted that geopolymer develops its full strength within a time (usually 7 days) much shorter than that for OPC.

Researchers have investigated the application of geopolymerization technology to produce geopolymer bricks and concrete from different types of waste materials including mine tailings, fly ash, and cement kiln dust [19-22]. This research, for the first time, studies complete recycling and utilization of waste concrete to produce geopolymer concrete, by using the waste concrete fines (WCF) from crushed waste concrete together with class F fly ash (FA) as the geopolymer source material and RA as the aggregate.

1.2 Research objectives

The major goal of the research is to investigate complete recycling and utilization of waste concrete to produce geopolymer concrete. Specifically, the research has the following objectives:

- Systematically study the macro-scale behavior of geopolymer concrete from completely recycled waste concrete by conducting mechanical tests to investigate the effect of different factors.

- Investigate the micro/nano-scale structure and characteristics of geopolymer concrete from completely recycled waste concrete at different conditions.
1.3 Research methodology

This research takes an innovative multi-scale and multi-disciplinary approach consisting of both experimental and numerical investigations as shown in Fig.1.

![Flow chart of the research methodology.](image)

1.3.1 Macro-scale study

The macro-scale study was focused on the effect of different factors on the mechanical behavior of geopolymer concrete (GPC) produced from completely recycled waste concrete. Uniaxial compression tests were performed to measure the UCS of GP paste and GPC prepared at different conditions. For GP paste specimens, the NaOH concentration, Na$_2$SiO$_3$ solution to NaOH solution (SS/N) mass ratio, and WCF content were adjusted to investigate how these factors affect the UCS of GP paste. For GPC specimens, different NaOH concentrations, cement (WCF and FA) to aggregate (C/A) ratios, water to cement (W/C) ratios, SS/N ratios and aggregate types (NA/RA) were used in order to study the effect of these factors on the UCS of GPC.
Four-point bending tests were conducted to measure the bonding strength of the ITZs between various pastes and aggregates. Different sandwich specimens were made to simulate these ITZs. The W/C ratio was adjusted to investigate how it affects the bonding strength.

1.3.2 Micro-scale study

The macro-scale behavior is closely related to the micro/nano-scale characteristics. The micro/nano-scale study evaluates how the chemical components in the recycled waste concrete, especially the calcium compounds, affect the composition and properties of the geopolymer products. X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX), and Fourier transform infrared spectroscopy (FTIR) were used in the micro-scale investigation.

The XRD analysis was conducted to quantify the phase state of materials before and after geopolymerization. A Scintag XDS 2000 PTS diffractometer using Cu Kα radiation, at 2.00 degree/min ranging from 10.00 to 70.00 degrees with 0.600 second count time was used to study the starting materials and the geopolymerization products. The SEM imaging and EDX analysis were performed in SE conventional mode using the FEI INSPEC-S50/Thermo-Fisher Noran 6 microscope. The SEM imaging investigates the development of the micro/nano-structure and the EDX analysis studies the surface constituting elements and evaluates the Si/Al and Na/Al ratios of different phases in the geopolymer matrix. The FTIR spectroscopy is used to investigate the difference in the chemical bonds of all the materials before and after geopolymerization. The spectra were obtained using the Thermo Nicolet 370 FTIR / EZ Omnic using a smart performance ATR ZnSe crystal. The spectrometer covers wavelengths from 600 to 4000 cm⁻¹.
1.4 Dissertation Layout

This dissertation is organized following the University of Arizona’s Graduate College Manual for Theses and Dissertations and includes two chapters followed by five appendices. The first chapter describes the background, research objectives, research approach and the layout of the dissertation. The second chapter summarizes the main findings of this research presented in the appendices. Appendix A is a published paper in which the feasibility of using the combination of waste concrete powder (also called waste concrete fines – WCF) and class F fly ash to produce a cementitious binder through geopolymerization is investigated. It focuses on studying the effect of calcium on the geopolymerization process of the properties of the geopolymer binder. Appendix B investigates the bonding strength of different types of interfacial transition zones (ITZs) through four-point bending tests. The focus of the study is to show that a good bonding between geopolymer paste and recycled aggregates can be achieved. Appendix C, based on the studies in Appendices A and B, investigates the feasibility of using both the waste concrete fines and the recycled aggregates from the waste concrete crushing process to produce new geopolymer concrete. The focus of this investigation is on 100% recycling of waste concrete through geopolymerization. Appendix D is a published paper in which aluminum sludge is used to improve the mine tailings-based geopolymer. This study identifies the optimum silica to aluminum molar ratio and the optimum sodium to aluminum molar ratio in order to acquire a high mechanical performance geopolymer. This research is not directly on waste concrete but provides useful information for better design of complete recycling and utilization of waste concrete through geopolymerization. In Appendix E, molecular dynamics simulations were performed to study the effect of calcium on the geopolymerization process and the properties of the geopolymer product. The molecular structure of sodium based geopolymer was first constructed and the sodium in the
geopolymer system was then replaced by calcium at different percentages in order to study the contribution of calcium to geopolymerization.
CHAPTER 2

PRESENT STUDY

2.1 Research performed

The methods, results, and conclusions of this research are presented in the appendices. Appendices A and D are two papers which have been published. Appendices B, C, and E present the most recent findings of this research, and the results are ready to be submitted for publication.

The objective of this research is to study complete recycling and utilization of waste concrete through geopolymerization. As mentioned in Chapter 1, WCF can be used together with class F fly ash as the geopolymer cementitious material and RA as the aggregate. It is very important to study the different factors that can affect the properties of geopolymer concrete (GPC), and then develop the optimum condition for production of GPC from waste concrete. In Appendix A, the feasibility of using WCF together with FA to produce geopolymer binder is studied. Various NaOH concentrations, SS/N ratios, and WCF contents were used to produce geopolymer paste specimens in order to study their effect on the properties of geopolymer paste. Uniaxial compression tests were conducted and SEM/EDX, XRD, and FTIR analyses were performed. Finally, the optimum condition for producing geopolymer binder was developed. Based on the study in Appendix A, the bonding strength of different types of ITZs was studied in Appendix B by performing four-point bending tests. Based on the measured bonding strength values for NA- and residual OPC paste/mortar (ROPM)-based ITZs, the bonding strength of the GP-RA and OPC-RA ITZs was estimated by considering the average area coverage of ROPM on the RA surface. SEM imaging was also performed to study the microstructure of the different ITZs. In Appendix C, GPC specimens were made and studied by using WCF/FA-based geopolymer as binder and RA
and NA as aggregate separately. Various NaOH concentrations, SS/N ratios, and C/A ratios were used to produce GPC in order to study their effect on the behavior of GPC. Appendix D outlines the study of how Si/Al and Na/Al molar ratios affect the mechanical properties of geopolymer. In the research aluminum sludge is added to mine-tailing based geopolymer products to adjust the Si/Al and Na/Al molar ratios. This research is performed in order to provide useful information for optimizing the design on complete recycling and utilization of waste concrete to produce new GPC. Finally, molecular dynamics (MD) simulations were performed to study the effect of calcium content on the microstructure and mechanical properties of sodium aluminosilicate geopolymer in Appendix E. The sodium in the geopolymer system was replaced by calcium at 25, 50, 75 and 100%, respectively. Uniaxial compression tests were conducted through the MD simulation, and the results were compared with those of macro-scale physical experiments.

2.2 Conclusions

The significant conclusions from this research are summarized below.

A) (Appendix A) The utilization of WCF together with FA can increase the UCS of the geopolymer binder up to 50% WCF content. Further increase of WCF decreases the UCS of geopolymer binder. The results indicate that by using 10 M NaOH solution, SS/N of 2 and 50% WCF, the highest geopolymer paste strength can be acquired. With proper combination of waste concrete fines and fly ash, the geopolymer binder with required strength can be produced.

B) (Appendix B) The water to cement (W/S) ratio has an important effect on the bonding strength of the different ITZs. Higher W/S ratio decreases the bonding strength of the GP-based ITZs and the OPC-NA ITZ, however the bonding strength of the OPC-ROPM ITZ
increases with higher W/S. The 14-day bonding strength is slightly higher than the 7-day bonding strength for both the GP- and OPC-based ITZs. And the GP-based ITZ shows smaller strength improvement with time than the OPC-based ITZ because GP gains most of its ultimate strength within 7 days but OPC requires at least 14 days. The GP-RA ITZ shows higher strength than the GP-NA, OPC-NA and OPC-RA ITZs, implying the great potential to use RA to produce geopolymer concrete.

C) (Appendix C) The results show that when other conditions are the same, the GPC at C/A = 0.29 has longer initial setting time and lower UCS than the GPC at C/A = 0.22; the GPC at 10 NaOH concentration has shorter initial setting time and higher UCS than the GPC at 14 NaOH concentration; the RA-based GPC has shorter initial setting time but higher UCS than the NA-based GPC. The SS/N ratio affects both the initial setting time and UCS of GPC. Higher SS/N leads to longer initial setting time and higher UCS of GPC up to SS/N = 1.1; further increase of SS/N after SS/N > 1.1 leads to shorter initial setting time and lower UCS of GPC. The higher curing temperature favors the geopolymerization process and leads to higher strength of the GPC. Both the WCF and RA from the waste concrete crushing process can be used to produce geopolymer concrete with good mechanical properties and thus waste concrete can be completely recycled based on the geopolymerization technology.

D) (Appendix D) By adding 10% and 20% AS to MT, the Si/Al ratio is decreased from 3.38 to respectively 2.71 and 2.17, and the UCS at the optimum Na/Al ratio of 1.1 is increased from 28.5 MPa to respectively 34.9 and 44.8 MPa. The addition of AS along with utilization of appropriate amount of NaOH makes both the Si/Al and Na/Al ratios reach
the optimum values for geopolymerization, leading to higher degree of geopolymerization and more compact geopolymer microstructure.

E) (Appendix E) The MD simulation results show that replacing sodium in the geopolymer system by calcium can effectively improve the strength of the geopolymer product. The general trend is in good agreement with the macro-scale physical experimental results, although the strength value from the MD simulation is significantly higher than that from the macro-scale physical experiments.

2.3 Future research

The research has shown that waste concrete can be completely recycled and reused to produce new concrete through geopolymerization. This new type of concrete gives the civil engineering industry a solution to address the issue of large amount of waste concrete from repairing and upgrading the deteriorate infrastructures and offers a new type of concrete which consumes smaller amount of natural materials and releases less greenhouse gases than the commonly used OPC concrete. Although the work has advanced the state of the art, further research is desired, including:

- Nanoindentation tests should be carried out on geopolymer paste, RA surfaces (both before and after geopolymerization) and GPC at different conditions to better understand the effect of different factors on the behavior of GPC produced from waste concrete.

- To fully investigate the effect of Ca on the geopolymerization process and the behavior of geopolymer products, the formation of calcium aluminum silicate hydrate (CASH) and calcium silicate hydrate (CSH) gels involving water needs to be considered. So the future research will be including water in the MD simulations of geopolymer containing Ca.
REFERENCE


APPENDIX A

PRODUCTION OF GEOPOLYMERIC BINDER FROM BLENDED WASTE CONCRETE POWDER AND FLY ASH

Paper has been published in the Journal of Construction and Building Materials

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ABSTRACT
Recycling and utilization of waste concrete is a significant contribution to environment and sustainable development. In current practice, the recycling of waste concrete is mainly limited to the use of crushed aggregates in low-specification applications. Few researchers have investigated complete recycling of waste concrete. These complete recycling methods, however, need to re-clinker the hydrated cement using the standard cement kiln procedures and thus consume significant amount of energy and release large quantity of CO₂. To completely recycle and utilize waste concrete in a sustainable and environmentally-friendly way, a method that does not need re-clinkering at high temperature should be used. This paper studies the production of geopolymeric binder from ground waste concrete (GWC) powder mixed with class F fly ash (FA), which can then be used with recycled concrete aggregates to produce new concrete. Specifically, the effect of composition and concentration of the alkaline solution and the content of GWC on the unconfined compressive strength (UCS) of the produced geopolymeric binder is investigated. SEM/EDX, XRD, and FTIR analyses are also performed to investigate the micro/nano-structure, morphology and phase/surface elemental compositions of the produced geopolymeric binder and the effect of calcium (Ca) on them. The results indicate that utilization of GWC together with FA can increase the UCS of the geopolymeric binder up to 50% GWC content. Further increase of GWC decreases the UCS of the geopolymeric binder. So with proper combination of GWC and FA, the geopolymeric binder with required strength can be produced.

Key words: Waste concrete, Fly ash, Geopolymer, CSH gel, Micro/nano structure, Unconfined compressive strength
1. Introduction

Concrete is the major construction material of infrastructure. Repairing and upgrading the deteriorating infrastructure systems will utilize large quantity of new concrete and in the meantime generate significant amount of waste concrete. Ordinary Portland cement (OPC) is commonly used as the binder in the manufacture of concrete. It is well known that the production of OPC not only consumes significant amount of natural resources and energy but also releases substantial quantity of greenhouse gases. To produce 1 ton of OPC, about 1.5 tons of raw materials is needed and 1 ton of CO$_2$ is released to the atmosphere [1-3]. Production of concrete also utilizes sand and aggregate. Quarrying operations for producing the sand and aggregate are energy intensive and can release high level of waste materials. The shortage of natural resources for construction materials in many regions has led to long-distance haulage and significantly increased costs [4-6]. Growing environmental awareness, the need to ensure sustainability of construction materials, and public concern to safeguard the countryside limit the use of quarrying sites and encourage the construction industry to look for alternative materials [6-10].

On the other hand, it is a great challenge to handle the significant amount of waste concrete to be generated from repairing and upgrading the deteriorating infrastructure systems [11-14]. For example, in the United States, concrete waste occupies one third of the volume of waste materials in landfills [14]. Besides, finding areas suitable for landfilling is getting harder and disposing is getting more expensive. Therefore, recycling of waste concrete is encouraged by different agencies and sought by various institutions. Although extensive research has been conducted [15-22], current recycling of waste concrete is still predominately limited to the use of concrete aggregates in low-specification applications such as base course and non-structural fill with the remainder still being landfilled [23,24]. When waste concrete is crushed, a certain amount of cement
paste/mortar from the original concrete remains attached to stone particles in the concrete aggregate. The attached paste/mortar is the main reason for the lower quality of the concrete aggregate than the natural aggregate. Compared to natural aggregates, the concrete aggregate has increased water absorption, decreased bulk density, decreased specific gravity, increased abrasion loss, increased crushability, and increased quantity of dust particles. The low quality of the concrete aggregate generally leads to new OPC concrete with inferior strength, durability, and shrinkage properties. Therefore, the utilization of concrete aggregates in structural concrete is very limited. In cases that the concrete aggregate is used together with natural aggregate for production of structural concrete, a limit of 30% of concrete aggregate is usually recommended [23-25]. Aggregate refining methods such as “heating and rubbing” [26] and “mechanical grinding” [27] have been developed for refining the quality of concrete aggregates by removing the attached paste/mortar; but these methods are energy intensive and produce additional fines which need to be disposed of. It is also noted that utilization of concrete aggregates as base course and non-structural fill may cause environmental problems such as contaminant leaching and pH changes in the surrounding soil and water [28-30].

Few researchers have investigated complete recycling of waste concrete [31,32]. These complete recycling methods, however, need to re-clinker the hydrated cement using the standard cement kiln procedures and thus consume significant amount of energy and release large quantity of CO₂. To completely recycle and utilize waste concrete in a sustainable and environmentally-friendly way, a method that does not need re-clinkering at high temperature should be used.

Recently, a new type of “cement”, called geopolymer or inorganic polymer, has been investigated by different research groups. Geopolymer is a synthetic alkali aluminosilicate material produced from the reaction of a solid aluminosilicate with a highly concentrated aqueous alkaline hydroxide
and/or silicate solution, having an amorphous to semi-crystalline polymeric structure. Geopolymer has many advantages over OPC and has been of great research interest as an ideal material for sustainable development. Different raw materials, which provide the silica and alumina source, have been used to produce geopolymers. The research has shown that the presence of calcium compounds in the raw material can improve the mechanical properties of geopolymer products due to the coexistence of the geopolymer gel and the calcium silicate hydrate (CSH) and calcium aluminum hydrate (CAH) gels [33-36].

Very limited research has been conducted on recycling waste concrete via geopolymerization. Yang et al. [37,38] produced geopolymer concrete by using recycled aggregates as partial replacement for the fresh ones and mixture of waste concrete powder and metakaolin along with silica fume as the source materials for the geopolymeric binder. Their study indicated that the content of metakaolin and silica fume and the raise in alkalinity lead to increase in compressive strength. Allahverdi and Kani [39] investigated geopolymerization of mixture of finely ground waste brick and concrete in different mix proportions. They demonstrated that higher brick content and alkalinity resulted in stronger geopolymeric binder and the final setting time reduced when higher alkalinity.

In order for waste concrete to be completely recycled, both the crushed aggregates and the fine powder fraction need to be utilized. This can be achieved by utilizing the crushed aggregates as the filler and the fine powder fraction (together with fly ash) as the geopolymer binder. In this method, the adherence between the crushed aggregates and the binder is not of concern anymore, since the old hardened cement attached to the crushed aggregates will participate in geopolymerization as a source of silicon (Si) and calcium (Ca) and result in a good bond between the new binder and the old aggregates. This paper mainly focuses on the feasibility of producing
geopolymeric binder using the mixture of ground waste concrete (GWC) powder and fly ash (FA) activated by sodium hydroxide (NaOH) and sodium silicate (SS) solution. The produced binder was investigated at different NaOH concentrations, SS to NaOH ratios (SS/N), and GWC contents to study the mechanical properties, micro/nano-structure, and phase/elemental composition, based on unconfined compression tests, scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) characterization, and X-ray diffraction (XRD) and Fourier Transform Infra Red (FTIR) analyses.

2. Materials and Methods

2.1. Materials

The materials used in this investigation include class F fly ash (FA), GWC powder, reagent grade 98% NaOH, aqueous SS, and de-ionized water. The class F fly ash was from Salt River Materials Group in Phoenix, Arizona. The GWC powder was obtained by crushing and grinding the tested OPC concrete specimens in the structural laboratory at the University of Arizona. Table 1 shows the elemental composition of the FA and the GWC powder based on the XRF analysis. It can be seen that the major constituents of the GWC powder are silica and calcium compounds with minor amount of alumina and iron oxide while in the FA, silica and alumina are the major and calcium and iron oxide are the minor constituents. The original concrete specimens were prepared with 14.5% (weight) type II Portland cement, 31.2% sand, 44.8% coarse aggregate, and 9.5% water. They were tested after 28 day curing in moisture room and the tested specimens were left for another 3 months in the air before crushed and mill ground (see next subsection for more details).

The particle size distribution of the GWC powder and the FA was determined using a Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer. Fig. 1 shows the particle size
distribution curves. The mean particle size of the GWC powder and the FA are respectively 18.0 and 13.5 μm with respectively about 80% and 90% particles finer than 75 μm. The specific gravity of the GWC and FA particles are respectively 2.53 and 1.97. Fig. 2 shows the SEM micrographs of the GWC powder and the FA. The GWC powder contains irregularly shaped particles with a rough surface while the FA particles are spheres with a smooth surface.

The NaOH flakes were obtained from Alfa Aesar Company in Ward Hill, Massachusetts. The NaOH solution was prepared by dissolving the NaOH flakes in de-ionized water. Aqueous SS \((SiO_2 = 29\%, Na_2O = 9\%, \text{and } H_2O = 62\%)\) with modulus \((SiO_2/Na_2O)\) of 3.22 was obtained from Fisher Scientific in Pittsburgh, Pennsylvania.

2.2. Experimental methods

After the 28 day-cured concrete specimens were tested and left in the air for another 3 months, they were crushed by a jaw crusher and separated into different parts based on the particle size. The part passing mesh 20 (0.853 mm) was subject to further grinding using a grinding mill to ensure that most particles pass mesh 200 (75 μm). The obtained GWC powder was mixed with FA at different proportions, 0, 25, 50, 75, and 100% (by the total mass of GWC powder and FA), to produce the geopolymer binder source material. The mixture of NaOH and SS solution was used as the alkaline activator. First, the NaOH solution was prepared by dissolving NaOH flakes in de-ionized water and stirred for at least five minutes. Considering the generated heat, the solution was allowed to cool down to room temperature and then mixed with the SS solution at a specified SS/N weight ratio and stirred for another five minutes. The resulted alkaline solution was kept in room temperature for half an hour and then slowly added to the GWC/FA mixture. The generated paste was stirred by a mixer for about five minutes to ensure sufficient dissolution of silica, alumina, and
calcium (Ca) in the alkaline solution. The viscosity of the produced pastes increased at higher NaOH and SS concentrations and greater GWC content. Depending on the alkaline solution concentration and GWC content, different water contents were used to reach consistent workability for the pastes. Table 2 shows the water contents for the specimens at different alkaline concentrations and GWC contents. The water content increases with higher NaOH concentration and greater GWC content.

The resulted paste was placed in cylindrical Plexiglas molds of 34.5 mm inner diameter and 86.3 mm length (i.e., an aspect ratio of 2.5). The mold was shaken by a vibrator during the casting to release the trapped air bubbles. The mold was capped and left in room temperature for curing. The specimens were de-molded after 24 hours and then placed in a plastic bag for 6 days’ curing before tested.

The NaOH solution was prepared at two concentrations, 5 and 10 M, and mixed with SS at SS/N ratios respectively of 1 and 2. At NaOH concentration of 5 M and SS/N = 2, the geopolymer paste was not sufficiently workable to be molded due to quick setting. Therefore, only the results for 10 M NaOH are reported at SS/N = 2.

Unconfined compression tests were performed on the cured cylindrical specimens with an ELE Tri Flex 2 loading machine at a constant loading rate of 0.1 mm/min to measure the unconfined compressive strength (UCS). The UCS was studied at different GWC contents, NaOH concentrations, and SS/N ratios. For each condition, at least three samples were tested and the average of the measured values was shown. Before conducting the compression test, the end surfaces of the specimens were polished to make sure they are accurately flat and parallel.

SEM/EDX was used to investigate the microstructure of the specimens and the morphology and elemental composition of the constituting matrix components. The SEM imaging/EDX analysis was performed in SE conventional mode using the FEI INSPEC-S50/Thermo-Fisher Noran 6 microscope.
The freshly failed surfaces from the unconfined compression tests, without polishing to keep the fractured surface “un-contaminated”, were used for the SEM imaging/EDX analysis. XRD was used to study the phase composition of the original material and the change due to the combined effect of geopolymerization and pozzolanic reactions. The XRD analysis was performed with a Scintag XDS 2000 PTS diffractometer using Cu Kα radiation, at 2.00 degree/min ranging from 10.00 to 70.00 degrees with 0.600 second count time. FTIR analysis was also performed to study the effect of geopolymerization and pozzolanic reactions on the materials’ chemical bonds before and after reaction. Spectra were obtained using Thermo Nicolet 370 FTIR / EZ Omnic using a smart performance ATR ZnSe crystal. The spectrometer covers wavelengths from 600 to 4000 cm⁻¹.

3. Results and Discussion

3.1. UCS

The study investigated the effects of the composition and concentration of the alkaline solution and the content of the GWC powder on the UCS of the geopolymer binder.

3.1.1. Effect of NaOH concentration

Fig. 3 shows UCS versus GWC content at NaOH concentration respectively of 5 and 10 M with SS/N = 1. The UCS values at 10 M NaOH concentration are higher than those at 5 M NaOH concentration. The increase of UCS with NaOH concentration can be explained by the fact that at higher NaOH concentration, larger amount of Na⁺ cations attack the surface of the solid phase leading to dissolution of more Si and Al and thus higher concentration of Si and Al in the liquid phase. Alkali activation of the raw aluminosilicate involves the chemical reaction between NaOH and the raw aluminosilicate by which the bridging oxygen (BO) atoms in the raw aluminosilicate
structure transform into non-bridging oxygen (NBO) atoms, which leads to isolation of the Si and Al atoms via the following scheme [40]:

\[
\text{Na}^+ - (\text{Al}^3\text{O}_2\text{Si})_{\text{raw}} + 2\text{Na}^+\text{OH}^- \rightarrow \text{Na}^+ - (\text{Al}^3\text{O}_2\text{Na}^+) + (\text{Na}^+\text{O}^-\text{Si})^- + \text{H}_2\text{O}
\]

(1)

According to this scheme, Na\(^+\) acts as a modifying (activating) and dissolving agent on both Si and Al, and thus the Na/Al and Na/Si ratios are important to display the availability of Na\(^+\) for Si and Al atoms, respectively. The Na/Al and Na/Si ratios in the current study range respectively from 0.21 to 1.39 and 0.10 to 0.26 (see Table 2). The two highest Na/Al and Na/Si ratios correspond to specimens 10-100-1 and 10-100-2, which were prepared with 100% GWC and synthesized with 10 M NaOH at SS/N ratios respectively of 1 and 2. Despite the highest ratios of Na/Al and Na/Si, these specimens exhibited the lowest UCS values indicating that in addition to the alkalinity, other factors such as Si/Al and Ca/Si ratios also significantly affect the reaction, which will be discussed later. However, at constant Si/Al and Ca/Si ratios, higher NaOH concentration will lead to dissolution of larger amount of Si and Al and result in higher UCS [41].

In addition to the dissolution function, Na\(^+\) also functions as charge balancing for 4-coordinated Al\(^{3+}\). A Na/Al ratio of about 1 is commonly recommended [42-44]. It is noted that the Na/Al ratios listed in Table 2 are for the initial materials and are not necessarily the same as the final ratios in the geopolymer gels.

The increase of UCS with NaOH concentration in the geopolymeric system was also noted by other researchers [39,45-47]. For example, Allahverdi and Khani [39] studied the production of geopolymer material from ground waste brick and concrete powders. They used NaOH at three
different levels, 6, 7, and 8% (by weight of the dry binder), and concluded that the increase of alkalinity resulted in shorter final setting time and higher strength. They also reported that the strength improvement with alkalinity was higher when the specimens contained more waste brick than concrete since the waste brick is more amorphous than the waste concrete. Similarly, in the present study, the elevated alkalinity resulted in larger increase of UCS when FA is the dominant fraction of the paste, i.e. when less than 50% GWC was used. This is because the FA particles are more amorphous than the GWC powder and thus more reactive to the alkaline solution (see Section 3.2 for more detailed discussion).

3.1.2. Effect of soluble silicate

Fig. 3 also depicts the effect of SS/N ratio on UCS at different GWC contents with 10 M NaOH concentration. The increase of SS/N ratio results in higher UCS at all GWC contents. Delayed setting and increased SiO$_2$/Na$_2$O ratio account for the increase of UCS with SS/N ratio. Delayed setting by addition of SS in the Ca-added geopolymer system was also noted by Pacheco-Torgal et al. [48]. They reported flash setting in tungsten mine tailings-based geopolymer at high NaOH concentrations when Ca(OH)$_2$ was added. This problem was resolved by increasing the SS/N ratio. Due to the high alkalinity and the fast dissolution of Ca-silicates, Ca(OH)$_2$ precipitates on the particle surface and prevents further dissolution of Si and Al. Addition of soluble silicates helps delay setting and thus more time is allowed for the dissolution of Si and Al. The other reason for the improving effect of SS on UCS is the availability of soluble silicates. Dissolution and hydrolysis of silica and alumina from the solid aluminosilicate source is the first step in geopolymerization. Hydrolysis of silica and alumina species involves formation of Si-OH and Al-OH bonds, which is followed by condensation. In a system where soluble silicate exists in the alkaline solution, the hydrolysis process is already accomplished and thus the geopolymerization
will take place faster. According to Silva et al. [49], hydrolysis of Si and Al from solid aluminosilicates takes place as the following:

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} + 2\text{OH}^- & \rightarrow 2[\text{Al(OH)}_4]^-
\text{SiO}_2 + \text{H}_2\text{O} + \text{OH}^- & \rightarrow [\text{SiO(OH)}_2]^-
\text{SiO}_2 + 2\text{OH}^- & \rightarrow [\text{SiO}_2(\text{OH})_2]^2-
\end{align*}
\] (2)

The hydrolysis of Si and Al is then followed by oligomerization and polycondensation. Polycondensation at low Si/Al ratios mainly happens between silica and alumina species leading to formation of poly-sialate (PS) while at high Si/Al ratios, first the silica species condense between themselves and then the formed silicate polymer condenses with the alumina species, which eventually result in formation of a 3D rigid geopolymeric network of PSS or PSD [49]. Addition of SS to the geopolymer mixture helps increase the Si/Al ratio in the reactive phase and thus form more rigid polymeric network.

Fig. 4a shows the variation of UCS with the initial Si/Al ratio. In order to display the effect of only the Si/Al ratio, the results corresponding to a limited range of Na/Al and Ca/Si ratios are shown in the figure. It can be seen that the UCS increases with the Si/Al ratio up to Si/Al about 3.38 and then decreases. Fig. 4b compares the results from the current study with those reported by other researchers. The general agreement between them is good, although the optimum initial Si/Al ratio (i.e. the Si/Al ratio at the largest UCS) from the current study is slightly higher than those reported by the other researchers. This is possibly because different source materials are used for the geopolymer. The results from other researchers in Fig. 4b are mainly related to metakaolin-based geopolymers. Since metakaolin is highly reactive, the final Si/Al ratio is likely close to the initial one. If the aluminosilicate source material contains considerable amount of un-reactive phase, there might be a notable difference between the initial Si/Al ratio and the final one which takes a
value from 1 to 3, depending on the oligomer types. For example, Klabprasit et al. [52] reported Si/Al = 8.0 as the optimum initial ratio for the rice husk-bark ash added FA-based geopolymer.

3.1.3. Effect of calcium

The addition of GWC, at both 5 and 10 M NaOH and SS/N = 1 and 2, improves UCS up to 50% GWC content and then results in UCS declination (see Fig. 3). The improving effect of GWC is greater at the higher SS/N ratio. The improving effect of GWC is mainly due to the provision of Ca and Si for the formation of CSH and geopolymeric gels. The presence of Ca in a geopolymeric system also accelerates dissolution and hardening due to the extra nucleation sites provided by Ca [53,54].

The improving effect of Ca on the geopolymeric system has been noted by different researchers [33,55-57]. Two mechanisms have been used to explain the contribution of Ca to the geopolymeric system. The first states that Ca$^{2+}$ acts as a charge-balancing agent and is integrated into the geopolymeric network via the following scheme [57]:

\[
\equiv\text{Si-O}^- + \text{Ca}^{2+} \rightarrow \equiv\text{Si-O}^-\text{Ca}^+ + \text{H}_2\text{O}
\]

\[
\equiv\text{Si-O}^-\text{Ca}^+ + \text{O}^-\text{Al} + \text{H}_2\text{O} \rightarrow [\equiv\text{Si-O-Ca-O-Al}] \rightarrow \equiv\text{Si-O-Al}^- + \text{Ca}^{2+} + 2\text{OH}^-
\]

(3)

The second states that Ca contributes to the formation of CSH gel which can coexist with the geopolymeric gel. In this case, the geopolymeric and CSH gels act as independent phases as also shown by Yip et al. [33] with the metakaolin-slag based geopolymeric system. The CSH gel as a product of geopolymeric or pozzolanic reaction can have different types depending on the concentration of Ca in the system. The CSH gel resulted from the hydration of Portland cement generally has Ca/Si = 1.7 – 1.8 although Ca/Si = 1.5 – 2 is also reported [57]. The CSH gel as a
co-product to the geopolymeric gel, however, has much lower Ca/Si ratios, generally smaller than 0.7 [33,57-59].

It is noted that the improving effect of Ca is limited to a certain amount of Ca in the geopolymeric system [33,36,60]. In the current study, the improving effect of GWC is limited to 50% added GWC. Further increase results in decrease of UCS. The adverse effect of GWC is mainly due to the precipitation of Ca(OH)$_2$ and too high a water content required for the sample preparation. Since the GWC particles are fine with high surface area, the Ca-silicate based coating layer dissolves quickly in the alkaline solution. The quick dissolution of calcium cations in the alkaline solution leads to fast elevation of Ca concentration in the solution until it exceeds the threshold concentration at the high pH and subsequently causes precipitation of Ca in the form of Ca(OH)$_2$. Too much precipitated Ca(OH)$_2$ increases the viscosity and makes it difficult to mold the specimen. In order to adjust the viscosity and achieve desired workability, extra water is required. To reach a consistent workability at higher GWC content, more water is required. Table 2 lists the water content used in this study which in general increases with the GWC content. Too much water in the paste results in porous microstructure due to evaporation of extra water and thus the decrease of UCS [61]. Furthermore, at high GWC content, the Ca-based precipitates create a coating film on both FA and GWC particle surfaces and consequently inhibit further dissolution of silica and alumina and hinder geopolymerization. This is similar to the phenomenon observed when too much SS is used in the alkaline solution.

Fig. 5 is reproduced from Fig. 3 to show the relationship between UCS and Ca/Si ratio. The data is presented at three different narrow ranges of Si/Al ratios in order to clearly show the effect of Ca/Si on UCS. The average Si/Al ratio of each range is respectively 2.37, 3.30, and 5.33. The first two averages are close respectively to the Si/Al ratio of PSS (poly sialate-siloxo) and PSD (poly
sialate-disiloxo) which have theoretical Si/Al ratio respectively of 2 and 3. It can be seen from Fig. 5 that the highest UCS’s are obtained at Si/Al = 2.80 - 3.81, which are close to the Si/Al ratio of PSD. The optimum Ca/Si ratios (corresponding to the highest UCS) are respectively 0.15, 0.18, and 0.25 for the average Si/Al ratios of 2.37, 3.30, and 5.33. This indicates that in Ca-added geopolymeric systems, the optimum Ca/Si ratio slightly increases with the Si/Al ratio, which is in agreement with the results from other researchers (see Fig. 6).

3.2. Micro/nano-scale investigation

The micro/nano structure, morphology and phase/surface elemental compositions of the geopolymer binders are investigated by SEM/EDX, XRD, and FTIR analyses.

3.2.1. SEM imaging /EDX analysis

Fig. 7 shows the SEM micrographs of the 0% GWC (100% FA) specimen synthesized at 10 M NaOH concentration and SS/N = 2 and cured at room temperature for 7 days. Three distinct phases can be clearly seen: the partially reacted FA particles, the glassy phase or the geopolymer gel which surrounds the FA particles, and the un-reacted FA particles which are embedded in the glassy gel.

Fig. 8 shows the SEM micrographs of the 50% GWC (50% FA) specimen synthesized at 10 M NaOH concentration and SS/N = 2 and cured at room temperature for 7 days. In addition to the phases seen in Fig. 7, there are three more phases: the CSH gel, the very little crystalline phase deposited on the FA particle surface, and the partially reacted GWC particles. Both the GWC and FA particles are attached by the glassy phase or the geopolymeric gel. The needle-shaped crystalline phase on the FA particle surface is less likely to be calcium compounds as the EDX analysis indicates that Si and Al are the major constituents. Therefore, the crystalline phase is
possibly due to minor crystallization of the aluminosilicate species. Cristelo et al. [64] also reported formation of the same type of crystalline structure on class F FA particle surfaces with similar elemental composition.

Table 3 compares the final Si/Al, Na/Al, and Ca/Si ratios obtained from the EDX analysis on the phases described above with the initial ones. In both the 0% and 50% GWC specimens, \((\text{Si/Al})_{RF} < (\text{Si/Al})_{GP} < (\text{Si/Al})_{UF}\), where RF, GP and UF stand respectively for (partially) reacted fly ash, geopolymer and un-reacted fly ash. The fact that \((\text{Si/Al})_{UF}\) is greater than the initial Si/Al ratio of the FA powder indicates that Al is likely to dissolve and migrate to the other phases. \((\text{Si/Al})_{UF}\) is also greater than \((\text{Si/Al})_{RF}\) possibly because only Al dissolves from the un-reacted FA particle surface while both Si and Al dissolve from the reacted FA particle surface. \((\text{Si/Al})_{RF} < (\text{Si/Al})_{GP}\) indicates that the concentration of Si in the geopolymer is higher than that in the interface between the geopolymer and FA particle. In other words, the transition phase in the FA-GP interface is weaker than the geopolymeric gel. The 50% GWC specimen has higher \((\text{Si/Al})_{GP}\) than the 0% GWC specimen. \((\text{Si/Al})_{GP} = 2.21\) and 3.74 respectively for the 0% and 50% GWC specimens. So the chemical composition of the geopolymer in the 0% and 50% GWC specimens is respectively close to the chemical composition of the PSS and PSD type geopolymer. In other words, the addition of calcium to the geopolymer system leads to formation of more rigid geopolymer. The 50% GWC specimen also has much higher Ca/Si ratio in the geopolymeric gel than the 0% GWC specimen, which indicates the incorporation of Ca in the geopolymeric network, as a charge-balancing cation as discussed earlier. As stated earlier, Ca is provided by dissolution of the coating layer on the GWC particles (see Fig. 2).

Fig. 9 shows the high magnification SEM micrograph and EDX analysis results on the labeled area in Fig. 2d. The GWC mainly contains crystalline particles, which are coated with a thin rough
layer. This layer is possibly the product of hydrated OPC along with some fine aggregates, which disappears after geopolymerization (see Fig. 8). This indicates the dissolution of the coating layer and incorporation in the geopolymerization. The EDX results confirm that the main constituent of the coating layer is Ca while the XRF analysis on the whole GWC indicates that Si and Ca are the main constituting elements. So the coating layer is mainly Ca(OH)$_2$ and CSH gel.

3.2.2. XRD analysis

Fig. 10 shows the XRD analysis results for the FA and GWC powders and the geopolymer specimens prepared with respectively 0% and 50% GWC, synthesized at 10 M NaOH and SS/N = 2, and cured at room temperature for 7 days.

The XRD pattern of the FA powder represents amorphous material with a diffused halo peak centered at about 22° along with a crystalline phase which consists of quartz (SiO$_2$) and mullite (Al$_{4.984}$Si$_{1.016}$O$_{9.508}$). The GWC powder is mainly crystalline material consisting of anorthite [Ca(Al$_2$Si$_2$O$_8$)], CSH gel [(CaO)$_x$.SiO$_2$.($\text{H}_2\text{O})_y$], portlandite [Ca(OH)$_2$], and quartz. In the GWC powder, anorthite and quartz originate from the powdered aggregates of the original concrete and the CSH gel and portlandite are the hydration products of the Portland cement. The CSH gel has characteristics reflections at 3.04, 2.79, and 1.82 Å, respectively corresponding to (2 2 0), (4 0 0), and (0 4 0) planes of 1.1-nm tobermorite [65-68]. Beside the crystalline phase in the GWC powder, there is a weak amorphous phase which extends from about 25° to 40°.

The geopolymerization has two main effects on the XRD patterns. First, the broad hump in both the 0% and 50% GWC specimens becomes wider and its center shifts toward larger angles, indicating formation of new amorphous material. The amorphous hump extending from about 20° to 40° is characteristic of the geopolymeric gel. The second effect is the decrease of the intensity
of the crystalline peaks, which indicates partial dissolution of the crystalline phase, especially for
the FA particles, as also evidenced by the SEM micrographs (see Figs. 7 and 8). In addition to the
partial dissolution, the decrease of the intensity of crystalline peaks can be due to the addition of
sodium silicate and consequently the increase of the SiO$_2$/Na$_2$O ratio [69,70].

Portlandite is the only crystalline phase in the GWC powder which undergoes full dissolution
after geopolymerization as the corresponding peaks in the GWC powder disappear in the 50%
GWC specimen. This is also confirmed by the SEM/EDX analysis as discussed earlier. However,
the CSH gel only undergoes partial dissolution. This indicates that the CSH gel and portlandite,
which are the main hydration products of Portland cement, do not exhibit the same reactivity to
the alkaline solution.

In the 50% GWC specimen a semi-crystalline phase is observed corresponding to the humps
centered at approximately 30 and 50°. This is due to the formation of low calcium CSH gel as also
demonstrated by Buchwald et al [34] with the slag added metakaolin based-geopolymeric system.
The formation of CSH gel in geopolymeric systems have been reported by many researchers
[33,34,63,65,71] although some researchers did not find any CSH gel in geopolymeric systems
even with Ca added [36,61,72,73]. For example, Mackenzie et al. [72] reported that the added Ca
was incorporated into the geopolymeric network. In the current study, based on the SEM/EDX and
XRD results, the added Ca can simultaneously be incorporated into the geopolymeric network and
contribute to the formation of the low calcium CSH gel. However, due to the high alkalinity, the
geopolymeric gel is the main product of the reaction.

3.2.3. FTIR Analysis
Fig. 11 shows the IR spectra of the FA and GWC powders and the geopolymer specimens prepared with respectively 0 and 50% GWC, synthesized at 10 M NaOH and SS/N = 2, and cured at room temperature for 7 days. The IR characteristic bands are summarized in Table 4.

All the powder and geopolymer specimens exhibit strong wide bands centered around 1000 cm$^{-1}$, which is attributed to the Si-O stretching vibrations of SiO$_4$ tetrahedra in the aluminosilicates [39,40,57,74,75]. For the GWC powder, the wide band centered around 970 cm$^{-1}$ is also attributed to the Si-O stretching vibrations of SiO$_4$ tetrahedra in the CSH gel [34,76,77]. The GWC spectra represent sharper bands than the FA spectra meaning that FA is more amorphous than GWC. This is also confirmed by the XRD analysis (see Fig. 10).

The main change in the IR spectra of FA and GWC after geopolymerization is related to the Si-O vibration bands, which undergo broadening and shifting toward a lower wave number. This is also noted by other researchers [73,75,80-82]. The peak broadening means transition to a less ordered structure due to formation of randomly distributed Si-Al bonds [75]. The transition of the Si-O related bands near 1000 cm$^{-1}$ to lower wave numbers is due to the transition of symmetric to asymmetric stretching mode of Si-O bonds, which follows depolymerization of silicates and substitution of some Si with Al [40,57,75]. Some researchers have also reported the shift of Si-O peaks toward greater wave numbers due to geopolymerization [61,78,82]. For example, Giannopoulou et al. [82] reported the shift toward higher wave numbers for geopolymerization of ferronickel slag but the shift toward lower wave numbers for red mud/metakaolin-based geopolymer. The Si-O stretching vibration of SiQ$^n$ units corresponds to the bands centered around 850, 900, 950, 1100, and 1200 cm$^{-1}$, respectively for n = 0, 1, 2, 3, and 4 [57]. For example, the Si-O vibration of SiQ$^3$ corresponds to 1100 cm$^{-1}$, which has the second highest degree of polymerization, but due to alkali activation, it shifts toward a lower wave number and then after
poly-condensation shifts toward a higher wave number. In the current study, both the 0% and 50% GWC geopolymer specimens exhibit shift toward lower wave numbers. The larger shifting in the 50% GWC specimen indicates higher extent of alkali activation in the calcium added geopolymer systems. This is also consistent with the final Na/Al ratios shown in Table 3, as larger number of NBO’s (non bridging oxygens) exist at Na/Al ratios larger than 1 [40], which is the case in the 50% GWC specimen. Besides that, a new weak and broad peak appears at 1400 cm$^{-1}$, which is due to the formation of new aluminosilicate phase related to geopolymerization [47]. This band is also stronger in the 50% GWC specimen. The decrease in the height of the band related to silicates after geopolymerization is due to the formation of CSH gel, which is more crystalline than geopolymer [83].

The other major change in the IR spectra of the original materials is related to the full dissolution of portlandite in the GWC powder, which disappear in the 50% GWC spectrum. The dissolution of portlandite is also confirmed with the XRD analysis as presented in the previous subsection.

4. Summary and Conclusions

The feasibility of utilizing GWC (together with class F FA) to produce geopolymer binder was studied. Specifically, the effect of GWC content, NaOH concentration, and SS/N on UCS was investigated. And the micro/nano-structure, morphology and phase/surface elemental compositions of the geopolymer binder were also studied by SEM/EDX, XRD, and FTIR analyses. Based on the experimental results, the following major conclusions can be drawn.

Inclusion of GWC helps improve the UCS of geopolymer binder up to a certain GWC content and further increase of GWC content leads to decrease of UCS. In the current experiment, 50% was found as the optimum GWC content at 5 and 10 M NaOH and with SS/N =1 and 2. The optimum
initial Ca/Si ratio (the Ca/Si ratio at the highest UCS) is low (0.15 to 0.25) for the GWC/FA geopolymer binder, which suggests formation of low-Ca CSH gel in the geopolymer system.

Increased NaOH concentration results in higher UCS, especially at GWC content less than 50%. Addition of SS also improves UCS due to provision of additional SiO₂ and delayed setting. The optimum initial Si/Al (the Si/Al ratio at the highest UCS) for the GWC/FA geopolymer binder is around 3.38.

The SEM/EDX, XRD and FTIR analyses confirm that the Ca in GWC enhances the strength mainly due to the formation of low Ca semi-crystalline CSH gel which coexists with the geopolymer gel and the incorporation of Ca⁺ into the geopolymer network as charge balancing cation.

The geopolymer in the GWC/FA geopolymer binder is close to PSD and thus stronger than the geopolymer in the pure FA geopolymer binder which is close to PSS.

5. Acknowledgements

This work is supported by the Environmental Research and Education Foundation (EREF). The authors gratefully acknowledge the Salt River Materials Group in Phoenix, Arizona for providing the fly ash used in this investigation.

6. References


Table 1. Chemical composition of ground waste concrete (GWC) powder and fly ash (FA) based on XRF analysis.

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>GWC (%)</th>
<th>FA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>40.1</td>
<td>57.5</td>
</tr>
<tr>
<td>CaO</td>
<td>20.6</td>
<td>6.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.6</td>
<td>29.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.5</td>
<td>2.95</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.3</td>
<td>NA</td>
</tr>
<tr>
<td>H₂O</td>
<td>2.2</td>
<td>NA</td>
</tr>
<tr>
<td>MgO</td>
<td>2.1</td>
<td>1.36</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Table 2. Chemical composition and conducted tests on the ground waste concrete (GWC)/fly ash (FA) specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>GWC (%)</th>
<th>NaOH Conc. (M)</th>
<th>SS/N</th>
<th>Water content (%)</th>
<th>Si/Al</th>
<th>Ca/Si</th>
<th>Na/Al</th>
<th>Na/Si</th>
<th>UCS Test</th>
<th>XRD</th>
<th>SEM</th>
<th>FTIR</th>
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<tr>
<td>GWC</td>
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<td>NA</td>
<td>NA</td>
<td>3.56</td>
<td>0.55</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>FA</td>
<td>0</td>
<td>NA</td>
<td>NA</td>
<td>1.67</td>
<td>0.11</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<tr>
<td>5-0-1*</td>
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<td>1</td>
<td>25.3</td>
<td>2.05</td>
<td>0.09</td>
<td>0.21</td>
<td>0.10</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-25-1</td>
<td>25</td>
<td>5</td>
<td>1</td>
<td>25.6</td>
<td>2.32</td>
<td>0.15</td>
<td>0.26</td>
<td>0.11</td>
<td>X</td>
<td></td>
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<tr>
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<td>5</td>
<td>1</td>
<td>32.0</td>
<td>2.87</td>
<td>0.22</td>
<td>0.41</td>
<td>0.14</td>
<td>X</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5-75-1</td>
<td>75</td>
<td>5</td>
<td>1</td>
<td>32.8</td>
<td>3.62</td>
<td>0.29</td>
<td>0.56</td>
<td>0.16</td>
<td>X</td>
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<tr>
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<td>1</td>
<td>36.2</td>
<td>5.26</td>
<td>0.37</td>
<td>0.94</td>
<td>0.18</td>
<td>X</td>
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<tr>
<td>10-0-1</td>
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<td>1</td>
<td>31.0</td>
<td>2.19</td>
<td>0.08</td>
<td>0.41</td>
<td>0.19</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10-25-1</td>
<td>25</td>
<td>10</td>
<td>1</td>
<td>28.1</td>
<td>2.42</td>
<td>0.15</td>
<td>0.44</td>
<td>0.18</td>
<td>X</td>
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<td></td>
</tr>
<tr>
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<td>1</td>
<td>28.6</td>
<td>2.86</td>
<td>0.22</td>
<td>0.57</td>
<td>0.20</td>
<td>X</td>
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<tr>
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<td>1</td>
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<td>3.81</td>
<td>0.28</td>
<td>0.94</td>
<td>0.25</td>
<td>X</td>
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<tr>
<td>10-100-1</td>
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<td>1</td>
<td>34.5</td>
<td>5.36</td>
<td>0.37</td>
<td>1.39</td>
<td>0.26</td>
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<td>2</td>
<td>24.27</td>
<td>2.36</td>
<td>0.08</td>
<td>0.28</td>
<td>0.12</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>2</td>
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<td>3.38</td>
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<td>4.12</td>
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<td>0.61</td>
<td>0.15</td>
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<td>2</td>
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<td>6.61</td>
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<td>0.19</td>
<td>X</td>
<td></td>
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* 5-0-1 represents specimen at 5 M NaOH concentration, 0% GWC and SS/N = 1.
Table 3. Comparison of the elemental compositions of the different phases shown in Figs. 7 and 8 obtained from EDX analysis with the initial ones before reaction.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Phase</th>
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<th>Na/Al</th>
<th>Ca/Si</th>
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<tr>
<td></td>
<td>GWC</td>
<td>3.89</td>
<td>0.21</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>10-100-2 combination</td>
<td>6.61</td>
<td>1.22</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>10-50-2 Combination</td>
<td>3.38</td>
<td>0.50</td>
<td>0.18</td>
</tr>
<tr>
<td>10-0-2</td>
<td>UF*</td>
<td>2.70</td>
<td>0.59</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>RF*</td>
<td>1.33</td>
<td>0.22</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>GP*</td>
<td>2.12</td>
<td>0.59</td>
<td>0.05</td>
</tr>
<tr>
<td>10-50-2</td>
<td>UF</td>
<td>3.96</td>
<td>0.55</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>RF</td>
<td>2.61</td>
<td>0.52</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>GP</td>
<td>3.59</td>
<td>2.34</td>
<td>0.32</td>
</tr>
</tbody>
</table>

* UF, RF, GP, and CR are respectively un-reacted, (partially) reacted, geopolymer, and crystalline phase (see Figs. 7 and 8).
Table 4. Infrared (IR) characteristic bands identified in fly ash (FA) and ground waste concrete (GWC) powders and the geopolymer specimens shown in Fig. 11.

<table>
<thead>
<tr>
<th>Wave Number (cm(^{-1}))</th>
<th>Characteristic bands</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>800-1,200</td>
<td>Si-O stretching vibrations of SiO(_4)</td>
<td>[34,39,40,74,75]</td>
</tr>
<tr>
<td>872</td>
<td>-CO(_3) vibrations in CaCO(_3)</td>
<td>[34,76]</td>
</tr>
<tr>
<td>970</td>
<td>stretching vibration mode of Si-O ((v_3)) in CSH gel</td>
<td>[34,76,77]</td>
</tr>
<tr>
<td>1,400</td>
<td>Si-O vibrations</td>
<td>[47]</td>
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<tr>
<td>1,650</td>
<td>bending ((v_2)) mode of H-O-H</td>
<td>[34,76]</td>
</tr>
<tr>
<td>2,350</td>
<td>C-O vibrations in CO(_2) constrained in amorphous phase</td>
<td>[78,79]</td>
</tr>
<tr>
<td>2,920</td>
<td>C-O vibrations in CO(_2) constrained in amorphous phase</td>
<td>[78,79]</td>
</tr>
<tr>
<td>3,645</td>
<td>O-H stretching vibration of portlandite</td>
<td>[34,76]</td>
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Fig. 1. Particle size distribution of fly ash (FA) and ground waste concrete (GWC) by laser diffraction.
Fig. 2. Low and high-magnification SEM micrographs of fly ash (FA) – (a), (b), and ground waste concrete (GWC) powder – (c), (d).
Fig. 3. UCS versus ground waste concrete (GWC) content (percent of total mass of FA and GWC) for specimens cured at room temperature for 7 days and synthesized at 5 and 10 M NaOH and SS/N = 1 and 2.
Fig. 4 (a) UCS versus initial Si/Al ratio from current study; and (b) Comparison of normalized UCS versus initial Si/Al ratio from current study and other researchers.
Fig. 5. UCS versus Ca/Si ratio at different ranges of Si/Al ratios from the current study.
Fig. 6. Comparison of initial Si/Al versus optimum Ca/Si (the Ca/Si at maximum UCS) from current study and other researchers.
Fig. 7. SEM micrographs of geopolymer specimen of 0% GWC (100% FA) synthesized at 10 M NaOH and SS/N = 2 and cured at room temperature for 7 days: (a) low magnification micrograph, (b) higher magnification micrograph of the labeled area in (a), (c) higher magnification micrograph of the labeled area in (b), and (d) micrograph of an un-reacted FA (GP: geopolymer, RF: partially or fully reacted FA, UF: un-reacted FA).
Fig. 8. SEM micrographs of geopolymer specimen of 50% GWC synthesized at 10 M NaOH and SS/N =2 and cured at room temperature for 7 days: (a) low magnification micrograph, (b) higher magnification micrograph of the labeled area in (a), (c) higher magnification micrograph of the labeled area in (b), (d) crystalline structure on un-reacted FA, and (e) EDX analysis result on the crystalline structure in (e) (GP: geopolymer, RF: partially or fully reacted FA, UF: un-reacted FA, CSH: calcium silicate hydrate gel, CR: crystalline phase).
Fig. 9. SEM/EDX analysis of the coating layer on the ground waste concrete (GWC) particle surface.

<table>
<thead>
<tr>
<th>Element Line</th>
<th>Weight (%)</th>
<th>Weight Error (%)</th>
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</thead>
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<tr>
<td>C K</td>
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<td>+/- 0.07</td>
</tr>
<tr>
<td>O K</td>
<td>43.06</td>
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</tr>
<tr>
<td>Na K</td>
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<td>Mg K</td>
<td>1.35</td>
<td>+/- 0.04</td>
</tr>
<tr>
<td>Al K</td>
<td>4.51</td>
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</tr>
<tr>
<td>Si K</td>
<td>17.55</td>
<td>+/- 0.11</td>
</tr>
<tr>
<td>Si L</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S K</td>
<td>0.63</td>
<td>+/- 0.05</td>
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<tr>
<td>S L</td>
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<tr>
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<td>K L</td>
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<td>---</td>
</tr>
<tr>
<td>Fe K</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Fe L</td>
<td>2.32</td>
<td>+/- 0.34</td>
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<tr>
<td>Total</td>
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</table>
Fig. 10. XRD patterns of FA and GWC powders and geopolymer specimens prepared with respectively 0% and 50% GWC at 10 M NaOH and SS/N = 2.0 and cured at room temperature for 7 days (A: anorthite, M: mullite, P: portlandite, Q: quartz, T: 1.1-nm tobermorite).
Fig. 11. IR spectra of FA and GWC powders and geopolymer specimens prepared with respectively 0% and 50% GWC at 10 M NaOH and SS/N = 2.0 and cured at room temperature for 7 days.
APPENDIX B

EXPERIMENTAL STUDY OF INTERFACIAL TRANSITION ZONES BETWEEN GEOPOLYMER AND RECYCLED AGGREGATES

Paper was prepared to submit to a journal

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Abstract

This paper experimentally studies the interfacial transition zones (ITZs) between geopolymer (GP) and recycled aggregates (RA). Considering that RA consist of the stone particles and the attached paste/mortar from the original ordinary Portland cement (OPC) concrete, both the ITZs between GP and natural aggregate (NA) and those between GP and residual OPC paste/mortar (ROPM) were studied. For comparison, the ITZs between OPC paste and NA and those between OPC paste and ROPM were also studied. The geopolymer was produced from waste concrete fines (WCF) and class F fly ash (FA) at a WCF/FA mass ratio of 1, using a mixture of 10 M NaOH solution and Na$_2$SiO$_3$ solution at a mass ratio of 2 as the alkaline activator. 4-point bending tests were conducted to measure the bonding strength of the different types of ITZs at a water to solid (W/S) of 0.30, 0.35 and 0.40 for the geopolymer and OPC pastes after 7 and 14 days curing, respectively. Scanning electron microscopy (SEM) imaging was performed to investigate the microstructure of the ITZs. The results indicate that when NA is used, the bonding strength of both the GP-NA and OPC-NA ITZs decreases with higher W/S ratio. This is mainly because higher W/S ratio leads to a more porous microstructure in the ITZ. When ROPM is used, higher W/S ratio leads to smaller bonding strength for the GP-ROPM ITZ but greater bonding strength for the OPC-ROPM ITZ. This phenomenon is mainly caused by the high water absorption capacity of ROPM. Based on the measured bonding strength values for NA- and ROPM-based ITZs, the bonding strength of the RA-based ITZs was estimated by considering the average area coverage of ROPM on the RA surface. The GP-RA ITZ has the highest bonding strength among the different ITZs, implying the great potential for utilizing waste concrete (both the WCF and the RA) to produce geopolymer concrete.
Keywords: Geopolymer; concrete waste; recycled aggregate; interfacial transition zone; bonding strength; 4-point bending test; microstructure
1. Introduction

Ordinary Portland cement (OPC) is widely used as a binder material in concrete production. The process of manufacturing OPC consumes a huge amount of source materials and also releases a tremendous quantity of greenhouse gases. Some to produce 1 ton of OPC, the industry consumes 1.5 tons of natural materials and releases 0.9 tons of CO₂ into the atmosphere [1,2]. The tremendous energy consumption during OPC production and the negative effects related to global warming have attracted more attention to the OPC industry. Due to the growing awareness of environmental protection and global warming issues, advocates have been pushing the construction industry to look for alternative materials [3-5]. On the other hand, the substantial amount of waste concrete from the repairing and upgrading of deteriorating infrastructures is becoming a challenging issue [6]. It is increasingly difficult to find appropriate places for disposal of waste materials. To address this issue, researchers are conducting extensive investigations for recycling and utilizing waste concrete. However, so far the utilization of waste concrete is still limited to low grade applications such as the construction of roadbeds and backfilling projects [7-16].

So far, very few researchers have attempted to recycle waste concrete completely. Some of them have repeated the OPC kiln procedures on waste concrete in order to acquire clinker. However, intense energy is required by this approach, and a large amount of CO₂ is emitted during the kiln procedures [17,18]. Recently Ahmari et al. [19] proposed a less energy consuming method to produce a new type of cementitious material through geopolymerization technology. They used a mixture of waste concrete fines (WCF) and class F fly ash (FA) as the source material and a mixture of high concentration NaOH solution (N) and soluble Na₂SiO₃ (SS) as the alkaline activator to produce geopolymer. By adjusting the WCF/FA mass and SS/N mass ratios, the Si/Al, Ca/Si and
Na/Al ratios were modified to study how different factors affect the strength of geopolymer (GP). The highest uniaxial compaction strength (UCS) of GP paste, about 35 MPa, was acquired at a 10 M NaOH solution, SS/N = 2 and WCF/FA = 1. The paste samples were cured at room temperature for seven days.

Based on the experimental results from Ahmari et al. [19], a hypothesis was proposed that the aggregates from the waste concrete crushing process can be used together with GP to geopolymer concrete with good mechanical properties. The recycled aggregate (RA) contains the residual paste/mortars (ROPM) from the original OPC concrete [see Fig. 1(a)]. Besides the original interfacial transition zones (ITZ) between ROPM and NA, two new types of ITZs, the one between GP and NA and the other between GP and ROPM, are formed in the new geopolymer concrete. The newly formed ITZs are important in determining the strength of the GP concrete.

In OPC concrete, the ITZ is the weakest link between aggregates and cement paste/mortar [20]. The stress level which can cause the failure of ITZ is significantly lower than that of either the aggregates or the paste/mortar, and as a result the ITZ determines the strength of the entire concrete [21]. Researchers [22-26] have conducted extensive research to study the bonding strength of ITZs between different types of cementitious materials and aggregates. Jiang [22] used class F fly ash to modify OPC and investigated the bonding strength of ITZ between the modified OPC and limestone aggregate. After curing for three days at 20±3 °C, the bonding strength varied from 1.65 to 2.31 MPa. Similarly, Guo et al. [23] used class F fly ash and ground granulated blast–furnace slag to modify OPC. They conducted bending tests to measure the bonding strength between the modified OPC and basalt aggregate. After curing for 91 days, the bonding strength ranged from 2.2 to 4.0 MPa. Besides the active mineral additions, some dispersible polymers were also added to the OPC to enhance the bonding strength of ITZ. For example, Jenni [24] added cellulose ether
and redispersible polymers which included VC (vinyl–acetate/ethylene/vinyl–chloride copolymer), SA (styrene/acrylic copolymer), EVA (ethylene/vinyl–acetate copolymer), and PVA (polyvinyl alcohol) into the OPC for modification. The bonding strength between the modified OPC and ceramic tile varied from 0.62 to 1.19 MPa. Lee and Deventer [25,26] studied the bonding strength of ITZs between original stone aggregates and geopolymer binders. They used class F fly ash/kaolin-based geopolymer binder and basalt/siltstone aggregates and conducted 3-point bending tests to measure the bonding strength. Their results show that the bonding strength of different ITZs varied from essentially 0 to 1.27 MPa.

This paper first measures the bonding strength of the ITZ between GP and NA and the ITZ between GP and ROPM using 4-point bending tests. Based on the measured bonding strength values of the two types of ITZs, the bonding strength of the ITZ between GP and RA was estimated by considering the average area coverage of ROPM on the surface of RA. For comparison, the bonding strength of the OPC-NA and OPC-ROPM ITZs were also measured and the bonding strength of the OPC-RA estimated. Besides, Scanning electron microscopy (SEM) imaging was performed to study the microstructure of the different ITZs.

2. Experiment study

2.1 Materials

The WCF was obtained by crushing the OPC concrete specimens already tested in the structures laboratory at the University of Arizona. These OPC concrete specimens were originally made by using 14.5% (weight) type II OPC, 31.2% fine aggregates, 44.8% coarse aggregates, and 9.5% water. Before crushed, they were left in normal room environment for three months. The Salt River Material Group in Phoenix, Arizona supplied the FA. The specific gravity of the WCF and FA are 2.53 and 1.97, respectively. Fig. 2 shows the particle size distribution of WCF and FA. 100% of
WCF and 90% of FA particles are finer than 75 μm. Table 1 shows the chemical composition of the WCF and FA obtained from XRF analysis. The FA contains significant amount of silicon and aluminum which are the main sources for the geopolymerization process. The WCF mainly contains silicon, calcium, and a little amount of aluminum. The type II OPC is from Oldcastle in Phoenix, Arizona.

The NA in this research was made by cutting natural limestone into rectangle slices at a size of 47.5 mm × 24 mm × 5 mm. The two large surfaces of the NA slice were filed to acquire the same roughness by using a grinding machine.

The regent level NaOH flake is from Alfa Aesar Company in Ward Hill, Massachusetts. The aqueous sodium silicate (SS) is from Fisher Scientific in Pittsburgh, Pennsylvania. There are 29% SiO₂, 9% Na₂O, and 62% H₂O in the aqueous SS and the SiO₂/Na₂O modulus ratio is 3.22. The NaOH flake was first dissolved in de-ionized water and then combined with the aqueous SS to make the alkaline activating solution.

2.2 Experimental design

The 4-point bending tests were performed to measure the bonding strength of GP-NA, OPC-NA, GP-ROPM, and OPC-ROPM ITZs. Fig. 3 shows the equipment used for the 4-point bending test with a beam specimen installed. The beam was prepared using a sandwich specimen and two precast OPC concrete sections as shown in Fig. 4. The sandwich specimens were made for testing different types of ITZs following the procedure below (see also Fig. 5):

(a) Test the ITZ between GP and NA: A 24 mm × 5 mm plastic strip was glued to one side of the stone slice to introduce an artificial crack. Then the rock slice was put into a mold where GP paste was poured in to cover both large side surfaces of the rock slice. After curing at room
temperature for specified period of time, the sandwich specimen was glued to the two precast OPC concrete beam sections by using epoxy resin. Finally, the 4-point bending test was performed on the resulting long beam as shown in Fig. 3. The obtained bonding strength of the ITZ is denoted as $\sigma_{\text{GP-NA}}$.

(b) Test the ITZ between GP and OPC: Repeated procedure (a) but used OPC instead of GP paste. The obtained bonding strength of the ITZ is denoted as $\sigma_{\text{OPC-NA}}$.

(c) Test the ITZ between GP and ROPM: A 47.5 mm × 24 mm × 24 mm OPC paste block was first produced by curing in a moisture room for 28 days at room temperature. The OPC paste block was then left in an ambient environment for another 15 days to make sure there was no residual water in the OPC block. A plastic strip with the same size as in procedure (a) was glued to one side of the OPC block. Then the OPC block was put into a mold where the GP paste was poured in to cover the surface with the plastic strip. After curing at room temperature for specified period of time, the sandwich specimen was glued to the two precast OPC concrete beam sections by using epoxy resin and then tested. The obtained bonding strength of the ITZ is denoted as $\sigma_{\text{GP-ROPM}}$.

(d) Testing the ITZ between OPC and ROPM: Repeated procedure (c) but used OPC instead of GP paste. The obtained bonding strength of the ITZ is denoted as $\sigma_{\text{OPC-ROPM}}$.

Based on the previous research [19], the GP paste was produced using a mixture of WCF and FA at a WCF/FA mass ratio of 1 as the source material and a mixture of 10 M NaOH solution and SS solution at SS/N = 2 as the alkaline activator. Three water to solid (W/S) ratios, 0.30, 0.35 and 0.40, were considered to in order to evaluate the effect of water content on the bonding strength of the different types of ITZs. Two curing times, 7 days and 14 days, were considered in order to evaluate the effect of curing time. Table 3 shows the detailed information on the sandwich
specimens at different conditions. Three specimens were prepared at each condition and the average of the three measured bonding strength values was used in the analysis.

The 4-point bending test was performed using an ELE Tri-Flex 2 loading machine at a constant loading rate of 0.1 mm/min. The distance between top and bottom two points is 115 and 230 mm respectively. The interface of the sandwich specimen is at the center of them. Based on the test, the bonding strength $\sigma$ of an ITZ was calculated by [27]:

$$\sigma = \frac{3F_l}{4bd^2}$$  \hspace{1cm} (1)

where $F$ is the maximum load that caused the failure of the beam, $l$ is the length between the bottom two points, and $b, d$ are the height and thickness of the beam (Fig. 4).

3. Results and discussion

3.1 Macro-scale properties

3.1.1. Bonding strength of NA-based ITZs

Fig. 6 shows the measured bonding strength of the GP-NA and OPC-NA ITZs at different W/S ratios and after 7 and 14 days’ curing, respectively. Both types of ITZs show lower bonding strength as the W/S ratio increases. This is mainly because higher W/S ratio which means more water causes more porous microstructure in the two types of ITZs, as shown later by the SEM images. The results also indicate that the GP-NA ITZ has higher bonding strength than the OPC-NA ITZ at the same W/S ratio.

The geopolymerization process of high calcium geopolymer systems can be schematically illustrated by the following two reactions [28]:
(i) Dissolution of SiO$_2$, Al$_2$O$_3$ and calcium sources (CaO and CaSO$_4$)

$$\text{SiO}_2 + \text{Al}_2\text{O}_3 \xrightarrow{\text{OH}^-} \text{SiO}_2(\text{OH})_2^{-2} \text{ or } \text{Si(OH)}_3^{-1} + \text{Al(OH)}_4^-$$  \hspace{1cm} (2)

$$\text{CaSO}_4, \text{CaO} \xrightarrow{\text{H}_2\text{O}} \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{OH}^-$$  \hspace{1cm} (3)

(ii) Precipitation reactions

$$\text{Ca}^{2+} + \text{SiO}_2(\text{OH})_2^{-2} \text{ or } \text{Si(OH)}_3^{-1} + \text{Al(OH)}_4^- \rightarrow \text{CASH gel}$$  \hspace{1cm} (4)

$$\text{Na}^+ + \text{SiO}_2(\text{OH})_2^{-2} \text{ or } \text{Si(OH)}_3^{-1} + \text{Al(OH)}_4^- \rightarrow \text{NASH gel}$$  \hspace{1cm} (5)

Water is released during the geopolymerization process and it is important to allow the water to quickly get out so that a dense microstructure forms in the geopolymer product [29-32]. At higher W/S ratios, the increasing amount of water will take a longer time to get out, and thus more micro-holes are generated in the geopolymer. The micro-holes are the source of micro-cracks which leads to decrease of the bonding strength of ITZs. On the other hand, although the hydration of OPC uses water, it is well known that the strength of OPC paste decreases with higher water content due to the formation of a more porous microstructure at higher water content. This is why the OPC-NA ITZ also showed lower bonding strength as the W/S ratio increased.

Fig. 6 also shows that the bonding strength of the two types of ITZs after 14 days’ curing is higher than that after 7 days’ curing, and the improvement for the OPC-NA ITZ is greater than that for the GP-NA ITZ. This is simply because the curing time of GP required to develop the strength is shorter than that of OPC. The fast strength development has been considered an important advantage of geopolymer products [33]. Research has shown that GP can gain a major portion of its ultimate strength within 2 days and essentially reach its ultimate strength within 7 days [29,30].
However, the time required for OPC to develop its ultimate strength is much longer than 7 days [34]. In general, 14 days’ curing is required for OPC to develop a major portion of its ultimate strength [35,36].

The GP-NA ITZ has higher bonding strength than the OPC-NA ITZ at the same W/S ratio simply because the GP paste is stronger than the OPC paste and GP-NA ITZ has a denser microstructure than the OPC-NA ITZ as shown by the SEM images to be presented later.

3.1.2. Bonding strength of ROPM-based ITZ

Fig. 7 shows the bonding strength versus W/S ratio for the GP-ROPM and OPC-ROPM ITZs after 7 and 14 days’ curing, respectively. As the GP-NA ITZ, the GP-ROPM ITZ shows smaller bonding strength as the W/S increases. This is simply because of the more porous microstructure of GP formed at higher W/S (thus more water content), as explained earlier. It is also noted that the GP-ROPM ITZ has higher bonding strength than the GP-NA ITZ (Fig. 6) at the same curing time and the same W/S. This is because ROPM absorbs more water/alkaline solution than NA, leading to less residual water/alkaline solution left in the GP of ROPM-based specimens. Besides, the alkaline solution absorbed into the ROPM dissolves some Si, Al and Ca from the ROPM, which is beneficial to the geopolymerization process. The dissolution can also partially geopolymerize the surface of the ROPM, leading to a stronger bonding between the GP and the ROPM.

On the contrast, unlike the OPC-NA ITZ, the OPC-ROPM ITZ shows higher bonding strength when the W/S ratio increases. This is possibly because as the W/S ratio increases, after the absorption of water by ROPM, more residual water is left in the OPC paste for the complete hydration process. The OPC-ROPM ITZs at W/S = 0.30 and 0.35 have lower bonding strength than the OPC-NA ITZs at the same W/S values but the OPC-ROPM ITZ at W/S = 0.40 has about
the same bonding strength as the OPC-NA ITZ at the same W/S value (comparing Figs. 6 and 7). This is simply because at W/S = 0.30 and 0.35, the residual water after the absorption by ROPM is not enough for the complete hydration process.

Similar to the NA-based ITZs, the ROPM-based ITZs after 14 days’ curing show higher bonding strength that those after 7 days’ curing, and the improvement for the OPC-ROPM ITZ is greater than that for the GP-ROPM ITZs.

3.1.3. Bonding strength of RA-based ITZs

As shown in Fig. 1, the surface of RA includes both the original NA and the ROPM. This means the bonding strength of a RA-based ITZ is contributed by both the NA-based ITZ and the ROPM-based ITZ. If the surface area coverage of RA by ROPM is defined as $R$, the bonding strength of RA-based ITZ, say the GP-RA ITZ, can be determined by:

$$\sigma_{\text{GP-RA}} = R\sigma_{\text{GP-ROPM}} + (1 - R)\sigma_{\text{GP-NA}}$$  \hspace{1cm} (6)

where $\sigma_{\text{GP-RA}}$ is the bonding strength of GP-RA ITZ to be estimated, and $\sigma_{\text{GP-ROPM}}$ and $\sigma_{\text{GP-NA}}$ are the measured bonding strength of GP-ROPM and GP-NA ITZs as discussed earlier, respectively.

Addas et al. [37] quantified the surface area coverage of RA by ROPM through image analysis and found that the average surface area coverage by ROPM ($R$) is 50.3%. Liu et al. [44] did similar studies and found an average $R$ equal to 48.1%. Using the average of the $R$ values from the two studies, 49.2%, the bonding strength of the GP-RA and OPC-RA ITZs were determined based on Eq. (6) and the results are shown in Fig. 8. For comparison, the measured bonding strength values of NA-based ITZs are also shown in this figure. The bonding strength of the GP-RA ITZ still follows the trend of the GP-NA ITZ: lower bonding strength at higher W/S. For the OPC-RA ITZ,
however, the decrease of bonding strength at higher W/S is much gentler than that for the OPC-NA ITZ, simply because higher W/S (which means more residual water after absorption by ROPM) is beneficial to the hydration process.

The OPC-RA ITZ has lower bonding strength than the OPC-NA ITZ. This is simply as expected and in agreement with existing research results. However, the GP-RA ITZ shows higher bonding strength than the GP-NA ITZ. This is probably due to the partial geopolymerization of the ROPM and the lower amount of water in the GP after absorption by ROPM, which improves the quality of both the RA and the geopolymer. This implies the great potential for utilizing waste concrete (both the WCF and the RA) to produce geopolymer concrete.

Fig. 9 summarizes the bonding strength values of different types of ITZs from various studies. The obtained bonding strength values of ITZs from the current study are in good agreement with those obtained by other researchers.

3.2 Micro-scale properties

In order to prove the assumption in previous sections, the stone slices from the OPC-NA test were collected and covered by GP by following the same procedure of making the OPC-NA specimen to produce the GP-RA specimens. After 7-day curing, SEM analysis was performed to observe the original ITZ of ROPM-natural stone and the new ITZ of GP-ROPM.

Fig. 10 shows the SEM micrographs of the OPC-NA and GP-NA ITZ specimens at W/S = 30%. The OPC-NA ITZ is very easy to be located because of the obvious micro-crack like structure along the edge of the NA. This type of micro-crack like structure leads to low bonding strength for the ITZ. Compared to the OPC-NA ITZ, the GP-NA ITZ is denser and more difficult to be located. This simply explains why the GP-NA ITZ has higher bonding strength than the OPC-NA ITZ.
Fig. 11 shows the SEM micrographs of the GP-RA ITZ specimen at W/S = 0.3 and the OPC-RA ITZ specimens at W/S = 0.3 and 0.4, respectively. The RA-based ITZs were produced by using the stone slices with attached OPC paste from the tested OPC-NA ITZ specimens following the procedure for making the GP-NA and OPC-NA ITZ specimens. It can be clearly seen that the GP-RA ITZ show much denser microstructure and is more difficult to be located than the OPC-RA ITZs. For the two OPC-RA ITZ specimens, more visible micro-crack like structure can be seen at W/S = 0.3 than at W/S = 0.4. This is possibly because the high water absorption capacity of RA has led to insufficient water available for hydration at W/S = 0.3 but about the right amount of water required for hydration at W/S = 0.4.

4. Conclusions

This investigation systemically studies the bonding strength of different ITZs at various conditions. Based on the study, the following conclusions can be drawn.

1) The water to cement (W/S) ratio has an important effect on the bonding strength of the different ITZs. Higher W/S ratio decreases the bonding strength of the GP-based ITZs and the OPC-NA ITZ due to the more porous microstructure at higher water content. However, the bonding strength of the OPC-ROPM ITZ increases with higher W/S because the water absorption of ROPM makes the amount of water available to be closer to the right amount of water required for hydration at higher W/S.

2) The 14-day bonding strength is slightly higher than the 7-day bonding strength for both the GP- and OPC-based ITZs. And GP-based ITZ shows smaller strength improvement with time than the OPC-based ITZ because GP gains most of its ultimate strength within 7 days but OPC requires at least 14 days.
3) The GP-RA ITZ shows higher strength than GP-NA, OPC-NA and OPC-RA ITZs, implying the great potential to use RA to produce geopolymer concrete.

Acknowledgements

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Reference


Table 1. Chemical composition (weight %) of waste concrete fines (WCF) and fly ash (FA).

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>WCF (%)</th>
<th>FA (%)</th>
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<tr>
<td>SiO$_2$</td>
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<td>CaO</td>
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Table 3. Composition of sandwich specimens prepared at different conditions.

<table>
<thead>
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<th>Specimen ID</th>
<th>ITZ type</th>
<th>W/S (%)</th>
<th>WCF (mass %)</th>
<th>FA (mass %)</th>
<th>OPC (mass %)</th>
<th>Curing time (day)</th>
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</tbody>
</table>

Note: In the specimen ID, NA = natural aggregate, GP = geopolymer, OPC = ordinary Portland cement, ROPM = residual OPC paste/mortar the first two digits mean the W/S ratio and the second two digits mean the curing days. In the table, ITZ = interfacial transition zone, WCF = waste concrete fine, and FA = class F fly ash.
Table 4. The interfacial transition zone (ITZ) bonding strength from the 4-point bending tests.

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>ITZ bonding strength σ (MPa)</th>
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</tr>
<tr>
<td>GP-ROPM-35-07</td>
<td>0.97</td>
</tr>
<tr>
<td>GP-ROPM-40-07</td>
<td>0.87</td>
</tr>
<tr>
<td>OPC-ROPM-30-07</td>
<td>0.52</td>
</tr>
<tr>
<td>OPC-ROPM-35-07</td>
<td>0.55</td>
</tr>
<tr>
<td>OPC-ROPM-40-07</td>
<td>0.68</td>
</tr>
<tr>
<td>GP-ROPM-30-14</td>
<td>1.31</td>
</tr>
<tr>
<td>GP-ROPM-35-14</td>
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</tr>
<tr>
<td>GP-ROPM-40-14</td>
<td>0.89</td>
</tr>
<tr>
<td>OPC-ROPM-30-14</td>
<td>0.58</td>
</tr>
<tr>
<td>OPC-ROPM-35-14</td>
<td>0.64</td>
</tr>
<tr>
<td>OPC-ROPM-40-14</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Note: In the specimen ID, NA = natural aggregate, GP = geopolymer, OPC = ordinary Portland cement, ROPM = residual OPC paste/mortar, the first two digits mean the W/S ratio (30 stands for 0.30) and the second two digits mean the curing days.
Fig. 1. (a) Recycled concrete aggregate with residual cement paste/mortar (ROPM) and interfacial transition zone (ITZ); (b) Geopolymerized recycled concrete aggregate.
Fig. 2. Particle size distribution of waste concrete fine (WCF) and fly ash (FA).
Fig. 3. 4-point bending test equipment and beam specimen.
Fig. 4. Experimental set-up (not to scale) of 4-point bending test on aggregate-paste sandwich specimen.
Fig. 5. Procedure for preparing sandwich specimens. NA = natural aggregate, OPC = ordinary Portland cement, GP = geopolymer, ROPM = residual OPC paste/mortar, $\sigma$ is the bonding strength of interfacial transition zone (ITZ).
Fig. 6. Bonding strength of GP-NA and OPC-NA ITZ cured for 7 days and 14 days. NA = natural aggregate, GP = geopolymer, OPC = ordinary Portland cement, W/S = water to solid ratio, and ITZ = interfacial transition zone. The numbers in the specimen ID stand for the curing days.
Fig. 7. Bonding strength of GP-ROPM and OPC-ROPM ITZ cured for 7 days and 14 days. ROPM = residual OPC paste/mortar, GP = geopolymer, OPC = ordinary Portland cement, W/S = water to solid ratio, and ITZ = interfacial transition zone. The numbers in the specimen ID stand for the curing days.
Fig. 8. Bonding strength of RA- and NA-based ITZs. NA = natural aggregate, RA = recycled aggregate, GP = geopolymer, OPC = ordinary Portland cement, W/S = water to solid ratio, and ITZ = interfacial transition zone.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>Cementitious material</th>
<th>Aggregate type</th>
<th>ITZ bonding strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>OPC mortars containing latex, cellulose ether, polyvinyl alcohol</td>
<td>Ceramic tile</td>
<td>0.0</td>
</tr>
<tr>
<td>B</td>
<td>Class F and kaolin-based GP mortar</td>
<td>Natural basalt and siltstone rock</td>
<td>0.5</td>
</tr>
<tr>
<td>C</td>
<td>OPC mortar containing class F fly ash</td>
<td>Natural granite</td>
<td>1.0</td>
</tr>
<tr>
<td>D</td>
<td>OPC mortar containing silica fume</td>
<td>Natural rock</td>
<td>1.5</td>
</tr>
<tr>
<td>E</td>
<td>OPC paste containing class I fly ash (Chinese standard)</td>
<td>Natural limestone</td>
<td>2.0</td>
</tr>
<tr>
<td>F</td>
<td>OPC mortar</td>
<td>Recycled concrete</td>
<td>2.5</td>
</tr>
<tr>
<td>G</td>
<td>OPC mortar containing silica fume</td>
<td>Recycled concrete</td>
<td>3.0</td>
</tr>
<tr>
<td>H</td>
<td>OPC mortars containing recycled rubble, brick, waste concrete</td>
<td>Red brick</td>
<td>3.5</td>
</tr>
<tr>
<td>I</td>
<td>OPC mortar containing recycled rubble, stainless steel and polypropylene fiber</td>
<td>Red brick</td>
<td>4.0</td>
</tr>
<tr>
<td>J1</td>
<td>WCF and class F fly ash based GP paste</td>
<td>Natural limestone</td>
<td>4.5</td>
</tr>
<tr>
<td>J2</td>
<td>OPC paste</td>
<td>Natural limestone</td>
<td>5.0</td>
</tr>
<tr>
<td>J3</td>
<td>WCF and class F fly ash based GP paste</td>
<td>Recycled concrete</td>
<td>5.5</td>
</tr>
<tr>
<td>J4</td>
<td>OPC paste</td>
<td>Recycled concrete</td>
<td>6.0</td>
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</tbody>
</table>

Fig. 9. Bonding strength of interfacial transition zones (ITZs) from different researchers.
Fig. 10. SEM micrographs of interfacial transition zones (ITZs) at W/S = 0.3: (a), (b) and (c): OPC-NA ITZ at different resolutions; and (d), (e) and (f): GP-NA ITZ at different resolutions. NA = natural aggregate, OPC = ordinary Portland cement, GP = geopolymer.
Fig. 11. SEM micrographs of interfacial transition zones (ITZs): (a), (b) and (c): GP-RA ITZ at W/S = 0.3; (d), (e) and (f): OPC-RA ITZ at W/S = 0.3; and (g), (h) and (i): OPC-RA ITZ at W/S = 0.4. OPC = ordinary Portland cement, GP = geopolymer, RA = recycled aggregate, ROPM = residual OPC paste/mortar. A: un-geopolymerized ITZ between ROPM and original stone, B: geopolymerized ITZ between ROPM and original stone.
APPENDIX C

EXPERIMENTAL STUDY OF GEOPOLYMER CONCRETE PRODUCED FROM WASTE CONCRETE

*Paper was prepared to submit to a journal*

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Abstract
This paper investigates the utilization of both the aggregates and fines from crushed waste concrete to produce new geopolymer concrete (GPC) so that waste concrete can be completely recycled. Based on previous studies and considering the workability of GPC, 25% waste concrete fines (WCF) and 75% class-F fly ash (FA) were used as the geopolymer cement source material and NaOH/Na$_2$SiO$_3$ solution as the alkaline activator. The research systematically studied the effect of NaOH concentration, Na$_2$SiO$_3$ solution to NaOH solution mass ratio (SS/N), and cement (WCF and FA) to aggregate (C/A) ratio on the behavior of GPC. The effect of water content and curing temperature on the initial setting time and the 7-day unconfined compressive strength (UCS) of the GPC was also studied. For comparison, GPC using natural aggregates (NA) was also produced and studied at similar conditions. The results show that the GPC produced from recycled aggregates (RA) has higher UCS than the GPC from NA at both room curing temperature and 35 ℃ curing temperature. This is possibly due to the stronger interfacial transition zones (ITZ) in the RA-based GPC than in the NA-based GPC considering that the absorption of the alkaline solution into the original paste/mortar on the RA can lead to partial geopolymerization of the original paste/mortar and the original ITZ. Based on this study, it can be concluded that waste concrete can be completely recycled based on the geopolymerization technology.

Key words: Waste concrete; Fly ash; Recycled aggregate; Geopolymer; Unconfined compressive strength.
1. Introduction

In recent decades, more and more infrastructures are deteriorating at an alarming rate, creating a critical situation in the United States. The American Society of Civil Engineering (ASCE) gave the nation’s infrastructure an overall grade of “D+” [6]. The whole civil engineering industry realize that repairing and upgrading these infrastructures is a great challenge which will require a huge amount of new construction materials.

Concrete is widely used in the construction and repair of infrastructure. Ordinary Portland cement (OPC) is commonly used as the binder in the manufacture of concrete. The process of producing OPC consumes not only a large amount of natural materials and energy but also releases a substantial quantity of greenhouse gases. Generally, in the process of producing 1 ton of OPC, 1.5 tons of resource material is consumed, and 0.9 ton of CO$_2$ is released into the atmosphere [2,3]. Beside the cement, production of concrete also requires sand and aggregates. Quarrying operations required to produce sand and aggregates are an energy-intensive process which also releases a significant amount of wastes. Further, the shortage of sand and aggregates in many parts of the U.S. leads to long-distance hauling and higher costs [4]. Growing awareness of environmental protection and global warming issues in recent years has been pushing the whole construction industry to look for alternative materials [5-7].

On the other hand, the significant amount of waste concrete generated from the process of repairing and upgrading deteriorating infrastructures becomes a great challenge. It is increasingly difficult to find suitable locations for disposing of the waste concrete. Therefore, different agencies and institutions have started to seek new methods for reusing waste concrete. Although much research has been conducted, so far the recycling of waste concrete is predominately limited to the utilization of concrete aggregates in low-specification applications such as base course and non-
structure filling [8-10]. When waste concrete is crushed, both aggregates (coarse and fine) and fines are produced. A certain amount of cement paste/mortar from the original concrete remains attached to the stone particles in the concrete aggregates (called recycled aggregates – RA later). The low quality of the RA is mainly due to the attached paste/mortar. Compared to natural aggregates (NA), RA has higher water absorption, abrasion loss, crushability and quantity of dust particles, but lower bulk density and specific gravity. The low quality of RA generally leads to new OPC concrete containing RA with inferior strength, durability and shrinkage properties. Therefore, the utilization of RA in the production of new structural concrete is limited.

Researchers have investigated the utilization of RA to partially replace NA in the production of new OPC concrete. Tam et al. [11] studied the properties of new OPC concrete by using different amounts of RA and recommended a limit of 30% RA. They [12] continued the study by developing a two-stage mixing method to improve the strength of OPC concrete containing RA. The results show that using the two-stage mixing method, the strength of new OPC concrete containing 20% RA can be improved by 21%. Based on the study, they recommended 25% to 40% of RA could be used in the production of new OPC concrete. González-Fonteboa et al. [13] tried to pre-wet RA for 10 minutes before the concrete mixing to keep the consistency. By doing so, they concluded that when 20% of coarse NA is replaced by RA, the stress–volumetric strain curves and critical stress values of the new OPC concrete are similar to those of the OPC concrete containing 100% NA.

Researchers have also developed aggregate refining methods to improve the quality of RA by removing the attached paste/mortar, including “heating and rubbing” [14], “mechanical grinding” [15] and “microwave heating” [3]. However, these methods are energy intensive and produce additional fines which need to be disposed of [16]. Obviously, an ideal solution is complete
recycling and utilization of waste concrete (both RA and fines) in the production of new structural concrete.

Very few researchers have investigated complete recycling of waste concrete. Tomosawa and Noguchi [17] combined OPC, crushed limestone and limestone dust to produce 100% recyclable concrete. Since the limestone is the only filler in the concrete, the concrete can be crushed and then calcined at very high temperature. The resulting clinker was then added with a suitable amount of gypsum and milled to produce recycled cement. Costes et al. [18] also did research in recycling waste concrete completely. They concluded that the pure hydrated cement can be re-clinkered through the normal kiln process at 1,450 °C. So a method for separating cement, sand and aggregates was developed. By heating the crushed waste concrete to 700 °C, the adherence of hydrated cement to sand and aggregates was weakened. Then a ball milling machine was applied to separate the hydrated cement from sand and aggregates. The separated hydrated cement along with an additive if necessarily, was then re-clinkered to produce new cement. It can be seen that both methods consume a significant amount of energy and thus generate a tremendous amount of greenhouse gas. Therefore, to completely recycle waste concrete, an eco-friendly method which does not require the re-clinkering process at high temperature should be developed [7].

In recent years, a new technology called geopolymerization shows its advantages in recycling different types of wastes to produce new construction materials. Geopolymer is a product from the reaction of solid aluminosilicates with a high concentration alkaline hydroxide and/or silicate solution. Zhang and his research group have investigated the application of this technology to produce geopolymer bricks and cement from different waste materials including mine tailings, fly ash, cement kiln dust, and aluminum sludge [19-23]. They have studied complete recycling and utilization of waste concrete to produce new concrete based on the geopolymerization technology
and successfully used waste concrete fines (WCF) from crushed waste concrete together with class F fly (FA) ash to produce geopolymer paste [2]. They have also investigated the interfacial transition zone (ITZ) between WCF/FA-based geopolymer paste/mortar and recycled aggregates (RA) and showed that strong bonding between the geopolymer paste/mortar and RA can be achieved.

This paper investigates the production of geopolymer concrete (GPC) using WCF and FA as geopolymer cement source material and RA (both coarse and fine) as aggregate so that waste concrete can be completely recycled. Based on the previous study [2] and considering the workability of GPC, 25% WCF and 75% FA were used as the geopolymer cement source material and NaOH/Na$_2$SiO$_3$ solution as the alkaline reagent. The research systematically studied the effect of NaOH concentration, NaOH solution to Na$_2$SiO$_3$ solution ratio, cement to aggregate ratio, water content, and curing temperature on the behavior of GPC. For comparison, GPC using NA was also produced and studied.

2. Experiment study

2.1. Materials

The coarse and fine RA and WCF were obtained by crushing the OPC concrete specimens already tested in the structures laboratory at University of Arizona (UA). The concrete lab class produced the OPC concrete specimens using 15.3% (weight) type II OPC, 26.9% sand, 50.1% coarse aggregate and 7.7% water. These specimens were cured in a moisture room at 23$^\circ$C for different times and then tested. The 7- and 28-day UCS are 19.4 and 36.5 MPa, respectively. Before the tested specimens were crushed, they were left in normal room environment for 3 months. The class F fly ash (FA) was provided by Salt River Material Group in Phoenix, AZ. Table 1 shows the chemical composition of the WCF and FA used in this research. For comparison purpose, the same
NA and sand that was used in the OPC concrete specimens were also used to produce GPC. Fig. 1 shows the particle size distribution of the different materials.

The alkaline solution for the geopolymerization was the NaOH solution made by using deionized water to dissolve industrial level NaOH pills and the reagent level aqueous sodium silicate (SS). The NaOH pills were purchased from Hill Brothers Chemical Co., and their purity is 97.5\% - 99.5\%. The SS (SiO$_2$ = 29\%, Na$_2$O = 9\%, and H$_2$O = 62\%) with modulus (SiO$_2$/Na$_2$O) of 3.22 was obtained from Fisher Scientific.

2.2. Samples preparation and test methods

Two series of GPC based on the types of aggregates were produced, one using RA (both coarse and fine aggregates) and the other using NA (both coarse NA and natural sand). In order to compare the difference between the two types of GPC, the grading of the coarse and fine RA was selected to be about the same as that of the NA. The same cementitious source materials were used to produced both types of GPC. The previous research [2] showed that flash setting occurred when the WCF/FA ratio was higher than 50\%. So in this research the WCF/FA ratio = 25\% was selected in order to acquire good workability and high strength. By using this WCF/FA ratio, two cement/aggregate ratios (C/A), 0.22 and 0.29, were used to research how the cementitious material to aggregate ratio affects the workability and strength of GPC. Table 2 shows the amount of WCF, FA, course RA (or NA), and fine RA (or sand) used at these two C/A ratios, respectively. Similarly, two NaOH concentrations, 10 and 14 M, were also considered to investigate the effect of NaOH concentration on the workability and strength of GPC. Various Na$_2$SiO$_3$ solution to NaOH solution ratios (SS/N) from 0.77 to 2.0 were also involved in the sample making process to study the optimum SS/N ratio for the GPC. Figs. 2 and 3 show a comparison of the NaOH concentrations and SS/N ratios used in this study and those from other geopolymer concrete investigations,
respectively. Table 3 shows the detailed information for the GPC specimens prepared at different conditions. Since the water absorption of NA is much lower than that of RA, the water to cement ratio (W/C) in the GPC with NA at C/A = 0.29 was adjusted to 40% in order to acquire similar setting time.

The sample making process followed the guidance of ASTM C192. In the preparation of GPC, the WCF, FA and aggregates were mixed first for 5 minutes and then mixed with a designated amount of NaOH solution for 5 minutes. After a homogeneous mixture was acquired, Na₂SiO₃ was added to the mixture and mixing was continued for another 5 minutes. The obtained mixture was then poured into molds with a diameter of 3 inches and a height of 6 inches. For each proportion, 6 concrete specimens were made, 3 cured at room temperature (23 °C) and 3 at 35 °C. While curing, after first 24 hours, all molds were detached from the concrete specimens and the specimens were then sealed individually in plastic bags for continued curing. After curing for 7 days, the UCS test was conducted to measure the strength of each specimen following the ASTM guidance.

A separated set of specimens were made following the same process for evaluating the initial setting time. The initial setting time test was performed by measuring the penetration resistance at room temperature following ASTM C403.

3. Results and discussion

3.1. Initial setting time

The initial setting time results of all mix formulations in this research are shown in Fig. 4. The initial setting time of GPC varies from 21 min to 151 min which was affected by C/A ratio, NaOH concentration, SS/N ratio and aggregate type. Fig. 5 shows a comparison of the initial setting time from this research with those from others researches on geopolymer paste/concrete. A good
agreement can be seen between the initial setting time range of the GPC in this study and those of high calcium fly ash based geopolymer paste/concrete in other studies. This is because of the high calcium content in the WCF used in this study. It can also be seen that the high calcium fly ash based geopolymer paste/concrete in general has shorter initial setting time than the class F fly ash based geopolymer paste/concrete.

3.1.1. Effect of cement to aggregate (C/A) ratio

For the GPC produced with RA, when W/C, SS/N and NaOH concentration are the same, the initial setting time at C/A = 0.29 is longer than that at C/A = 0.22. Since the water absorption capacity of RA is high, the free liquid solution in the concrete mixture can be easily absorbed into RA. There is the same amount of RA in the two series of GPC with constant W/C ratio. Higher C/A, which is 0.29, means not only more cementitious materials but also more free liquid solution in the concrete mixture. The larger amount of free liquid solution lubricates the concrete mixture and extends the setting time. Similar phenomenon and analysis were also recognized by others in their concrete research [39-41]. Yurdakul [42] and Mindess et al. [42] also concluded from their research that the workability and setting time can be improved by supplementing additional cementitious materials such as fly ash, slag, calcined clay, metakaolin and shale. This is because the special fine spherical morphology of these supplementary cementitious materials can reduce the inter-particle friction.

3.1.2. Effect of NaOH concentration

In the geopolymerization process, some of the silicates in the cementitious source materials were dissolved by the NaOH solution and became one of the Si resources. The other Si resource was supplied by the Na₂SiO₃ solution directly. The other main element in the geopolymer framework is Al which was only supplied from the solid resource materials.
In the low calcium based geopolymer systems, the setting is determined by the formation of sodium aluminate silicate hydrate gel (NASH) [43,44]. When the concentration of Si is high, more silicate species are available to condense between themselves instead of with aluminate species. It is known that the rate of condensation between silicate species themselves is slower than that between silicate and aluminate species. As a result, when the silicate species are dominant in the geopolymer system, the setting time is longer. In contrast, when the aluminate species are dominant, the setting time is shorter. The most important difference between the high calcium and low calcium geopolymer systems is that a substantial amount of Ca$^{2+}$ is dissolved from the solid source materials. In this research, WCF contains a large amount of CaO and CaSO$_4$ which becomes available as a Ca resource for the geopolymer system. According to Chindaprasirt et al. [34], the possible dissolution and precipitation reactions of high calcium geopolymer systems can be schematically illustrated by the following two reactions:

(i) Dissolution of SiO$_2$, Al$_2$O$_3$ and calcium sources (CaO and CaSO$_4$)

\[
\text{SiO}_2 + \text{Al}_2\text{O}_3 \xrightarrow{\text{OH}^-} \text{SiO}_2(\text{OH})_2^{2-} \text{ or } \text{Si}(\text{OH})_3^{-1} + \text{Al}(\text{OH})_4^- \\
\text{CaSO}_4, \text{CaO} \xrightarrow{\text{H}_2\text{O}} \text{Ca}^{2+} + \text{SO}_4^{2-} + \text{OH}^- 
\]

(ii) Precipitation reactions

\[
\text{Ca}^{2+} + \text{SiO}_2(\text{OH})_2^{2-} \text{ or } \text{Si}(\text{OH})_3^{-1} + \text{Al}(\text{OH})_4^- \rightarrow \text{CASH gel} \quad (1) \\
\text{Na}^+ + \text{SiO}_2(\text{OH})_2^{2-} \text{ or } \text{Si}(\text{OH})_3^{-1} + \text{Al}(\text{OH})_4^- \rightarrow \text{NASH gel} \quad (2)
\]
Generally the calcium aluminate silicate hydrate gel (CASH) is stable when the pH value of the reaction environment is $>12$ at which reaction (1) is dominant in the setting process. The dissolution process of SiO$_2$ and Al$_2$O$_3$ consumes OH$^{-1}$ and leads to lower pH (9-12) value in the reactivity environment which allows reaction (2) to be dominant. The final strength develops in reaction (2). The setting process in the high calcium based geopolymer system is determined by the formation of both the NASH and CASH gels.

During the dissolution process, Al is easier than Si to be dissolved [34]. When the SS/N ratio and C/A are constant, less OH$^{-1}$ ions are available in the GPC mixture with 10 M NaOH solution than in the GPC mixture with 14 M NaOH solution. So fewer silicates were dissolved in the GPC mixture at 10 M NaOH than at 14 M NaOH. This is why the setting time of the GPC at 10 M NaOH solution was shorter than that of the GPC at 14 M NaOH.

3.1.3. Effect of SS/N ratio

As shown in Fig. 4, when the SS/N ratio is smaller than 1.1, the initial setting time of all GPC specimens increases with higher SS/N, reaching the longest setting time at SS/N = 1.1. After SS/N = 1.1, the initial setting time of all GPC specimens starts to decrease with higher SS/N. This is because when SS/N < 1.1, the increasing amount of silicate species from SS at higher SS/N leads to more condensation between silicate species themselves and thus longer setting time. When SS/N > 1.1, however, continuing increase of SS/N leads to significantly less amount of OH$^{-1}$ and the dominance of the precipitation reactions, thus resulting shorter setting time.

The SS/N ratio plays a vital role in the geopolymerization process and affects the initial setting time. Table 4 shows a summary of optimum SS/N ratios and NaOH concentrations from different studies for acquiring the longest setting time.
3.1.4. Effect of aggregate type

Fig. 4 clearly shows that 10-22RA specimens have much shorter initial setting time than 10-22NA specimens. This is mainly because RA absorbed more water and thus there was less free liquid in the RA GPC mixture which leads to shorter initial setting time. The other reason is because the surface of RA is more angular and rougher than the surface of NA (see Fig. 6). The surface conditions of RA caused extra friction during the mixing process which may have led to new fresh broken sections absorbing more water and finally decreasing the initial setting time. Similar conclusions were also summarized by several researchers [40-42].

3.2. UCS

Figs. 7 and 8 show the UCS of GPC specimens cured at 35°C and 23°C, respectively. The C/A ratio, NaOH concentration, SS/N ratio, aggregate type and curing temperature all affect the strength of GPC. Fig. 9 summarizes the UCS of GPC from different researchers. The obtained UCS values of GPC from this research are within the range of UCS values obtained by other researchers.

3.2.1 Effect of cement to aggregate (C/A) ratio

In both Figs. 7 and 8, when the NaOH concentration, curing temperature, SS/N and aggregate type are the same, the GPC specimens with the lower C/A ratio of 0.22 show higher strength than those with the higher C/A ratio of 0.29. For example, the UCS values of 14-22H(RA) specimens are always higher than those of 14-29H(RA) specimens. From the moment that the NaOH solution was added to the solid mixture, the RA started to absorb the liquid solution and continued absorbing for the whole mixing process. The absorption process also happened from the moment that the SS solution was added into the mixture. The same amount of RA was used at both C/A values, which means the liquid solution absorption capacity of RA was the same at both CA values.
Since the same W/C ratio was used at both C/A values, the higher C/A ratio means more liquid solution or water was available in the mixture after the aggregate absorption. Research has shown that higher water content in the geopolymerization process leads to lower strength of the geopolymer product. For example, Ahmari et al. [2] found that higher water content leads to more porous micro-structure in the geopolymer paste. During the geopolymerization process, the extra water occupies the space in geopolymer. After the curing process, this type of space develops into small holes due to the release of water. The small holes can lead to easier cracking and thus lower strength of the geopolymer paste. Zhang et al. [21] and Ren et al. [23] also found similar phenomenon in their geopolymer paste investigations.

For the GPC in this research, the larger amount of liquid solution not only caused the more porous structure of the mortar/paste but also adversely affected the ITZ. Ren and Zhang [24] studied the strength of ITZ between geopolymer (GP) paste and different types of aggregates. The results showed that the bonding strength between the GP-RA and GP-NA interfaces all decreased at higher water content. Both the more porous structure and the lower ITZ strength led to smaller UCS due to the more water content related to the higher C/A ratio.

An opposite trend can be seen in Figs. 7 and 8 when NA was used: the UCS of 10-29H(NA) specimens is higher than that of 10-22H(NA) specimens. This is simply because, as discussed previously, a lower W/C = 0.40 was used for 10-29H/R (NA) than that (0.45) for 10-22H/R(NA) in order to achieve a similar initial setting time. Considering the low water absorption capacity of NA, the UCS of NA-based GPC still followed a similar trend to that of the RA-based GPC: lower water content leads to higher UCS. This is in agreement with the results by other researchers [45-48].
3.2.2. Effect of NaOH concentration

Figs. 7 and 8 show that, when other parameters are the same, the GPC specimens with the lower NaOH concentration of 10 M have higher UCS than the GPC specimens with the higher NaOH concentration of 14 M. Generally there are two roles of NaOH solution in the geopolymerization: dissolving Si and Al species from source materials and supplying the Na\(^+\) to keep the charge balanced.

High OH\(^-\) concentration can accelerate the dissolution of silicates and aluminates from the source material, but also hinder the polycondensation. Zuhua et al. [49] summarized six possible reactions which show the role of water in dissolution and polycondensation (precipitation) processes as below:

\[
\begin{align*}
\text{Si-O-Si} + \text{H}_2\text{O} & \rightarrow 2\text{Si-OH} \quad (3) \\
\text{Al-O-Al} + \text{H}_2\text{O} & \rightarrow 2\text{Al-OH} \quad (4) \\
\text{Si-O-Al} + \text{H}_2\text{O} & \rightarrow \text{Si-OH} + \text{Al-OH} \quad (5) \\
\text{Si-OH} + \text{Al-OH} & \rightarrow \text{HO-Si-O-Al-OH} + \text{H}_2\text{O} \quad (6) \\
n(\text{OH})_3 - \text{Si-O-Al(OH)} & \rightarrow \text{Na}^+ \cdot (-\text{Si-O-Al-OH}) + 3n\text{H}_2\text{O} \quad (7) \\
n(\text{OH})_3 - \text{Si-O-Al-O-Si(OH)} & \rightarrow \text{Na}^+ \cdot (-\text{Si-O-Al-O-Si}) + 3n\text{H}_2\text{O} \quad (8)
\end{align*}
\]

In reactions (3) – (5), water is required to dissolve the Si and Al. More water can accelerate the dissolution of Si and Al when the OH\(^-\) concentration is high enough. At the same W/C ratio, the
10 M NaOH solution contains more water than the 14 M NaOH and thus leads to more Si and Al dissolved for forming geopolymer. On the contrast, in reactions (6) – (8), water is the product of the reactions. Too much water hinders the polycondensation process. The 14 M NaOH solution supplies more NaOH for the polycondensation process than the 10 M NaOH solution and thus generates more water. The larger amount of water generated during reactions (6) – (8) leads to a looser structure and thus lower UCS of the GPC at 14 M than at 10 M.

3.2.3. Effect of SS/N ratio

Figs. 7 and 8 shows that the UCS of both the RA- and NA-based GPC increases with higher SS/N up to SS/N = 1.1 and then starts to decrease with higher SS/N.

Garcia-Lodeiro et al. [50] investigated that NASH gel precipitated when the pH value was between 9.5 and 12.0. They found that in this pH environment the NASH gel can fully convert into CASH gels if there was enough available Ca\(^{2+}\). When SS/N < 1.1, the OH\(^{-}\) concentration is high enough for the dissolution of Si, Al and Ca. As SS/N increases, the available OH\(^{-}\) after the dissolution reactions decreases, leading to decrease of the pH value of the GPC mixture. After the pH is dropped to below 12 and enough Ca\(^{2+}\) is available in the geopolymer mixture, the NASH gel starts to accept Ca through ion-exchange and form CASH gel. The CASH gel formed from ion-exchange retains the 3D aluminatesilicate framework [51] and effectively improves the UCS [52,53]. Yip et al. [54] concluded that the role of this type of CASH gel is like a micro-aggregate which produces denser and more uniform matrices leading to higher strength. However, after SS/N > 1.1, continuing increase of SS/N leads to less NaOH available in the GPC mixture and thus less amount of Si, Al and Ca dissolved from the source material. Even if the pH value is lower than 12, there is not enough Ca\(^{2+}\) to form the CASH gel, leading to lower UCS at higher SS/N ratio.
Table 5 summarizes the optimum NaOH concentrations and SS/N ratios from different studies used to generate the highest 7-day strength of geopolymer concrete.

3.2.4. Effect of aggregate type

Figs. 7 and 8 clearly show that, when all other conditions are the same, the RA-based GPC has much higher UCS than the NA-based GPC. It can also be seen that within the SS/N range of 0.9 – 1.4 the effect of SS/N on the UCS of RA-based GPC is much greater than that on the NA-based GPC. To be clearer, Fig. 10 shows a direct comparison of the UCS values of the two types of GPC at SS/N = 1.1.

As discussed earlier, when the C/A and W/C ratios are the same, RA absorbed more free liquid solution than NA, leading to less residual alkaline solution in the RA-based GPC mixture than in the NA-based GPC mixture and thus higher UCS of the RA-based GPC than the NA-based GPC. Generally less water content can improve the strength effectively, as shown by researchers in the investigation of OPC concrete [41,42] and geopolymer concrete [55-57]. For example, Lizcano et al. [57] studied the effect of water content on the structure of metakaolin-based geopolymer and concluded that water content is a major factor affecting the density and open porosity of geopolymer, higher water content leading to lower density and higher porosity of the geopolymer. Based on these findings several investigations were conducted by using a superplasticizer to reduce the water content in order to acquire better workability and higher strength [58-61].

The effect of the aggregate type on the UCS is also related to the surface condition of RA and NA. As shown in Fig. 6, the RA surface is rougher and more angular than the NA surface. The surface texture of RA favors the bonding between the RA and the geopolymer cementitious material. On the RA surface, some original paste/mortar remains attached to the original rock.
between the attached paste/mortar and the original rock affects the strength of the GPC. However, because of its high porosity, the attached paste/mortar can absorb the alkaline solution, leading to partial geopolymerization of not only the attached paste/mortar itself but also the original ITZ. This process improves the quality of RA and favors the strength of the final GPC. The high alkaline solution absorption of RA also improves the new ITZ between the RA (including the original stone and the attached original paste/mortar) and the geopolymer binder. The less amount of alkaline solution remained in the geopolymer cementitious material due to the high absorption of RA also favors the formation of denser new ITZ. On the opposite, due to the low water absorption of NA, the new ITZ between NA and geopolymer binder is loose. Fig. 11 clearly shows the difference between the GP-RA ITZ and the GP-NA ITZ.

In the SS/N range of 0.9 to 1.1, the change of SS/N has much greater effect on the UCS of RA-based GPC than on the UCS of NA-based GPC. This is simply because the change of SS/N has much greater effect on the RA than on the NA regarding both the dissolution/precipitations reactions and the formation of ITZs.

3.2.5. Effect of curing temperature
Comparing Figs. 7 and 8, it can be clearly seen that when other conditions are the same, the UCS of GPC at 35°C curing temperature is much higher than that of GPC at room temperature curing (23°C). This is what expected because in general the strength of geopolymer increases with higher curing temperature up to a certain temperature, say 75°C and 90°C [62-64].

4. Conclusions
This paper presents the results of a study on complete recycling and utilization of waste concrete to produce new structural concrete through geopolymerization. Based on the investigation, the following conclusions can be drawn:

1) When all other conditions are the same, the GPC at C/A = 0.29 has longer initial setting time and lower UCS than the GPC at C/A = 0.22.

2) When all other conditions are the same, the GPC at 10 NaOH concentration has shorter initial setting time and higher UCS than the GPC at 14 NaOH concentration.

3) The SS/N ratio affects both the initial setting time and UCS of GPC. Higher SS/N leads to longer initial setting time and higher UCS of GPC up to SS/N = 1.1; further increase of SS/N after SS/N > 1.1 leads to shorter initial setting time and lower UCS of GPC. So the optimum SS/N which results in the longest initial setting time and the highest UCS of GPC is 1.1 which is in general agreement with results obtained by other researchers.

4) When all other conditions are the same, the RA-based GPC has shorter initial setting time but higher UCS than the NA-based GPC.

5) The higher curing temperature favors the geopolymerization process and leads to higher strength of the GPC.

6) Both the WCF and RA from the waste concrete crushing process can be used to produce geopolymer concrete with good mechanical properties and waste concrete can be completely recycled through the geopolymerization technology.

Acknowledgements

This work is supported by the Environmental Research and Education Foundation (EREF). The authors gratefully acknowledge the Salt River Materials Group in Phoenix, Arizona for providing the fly ash used in this investigation.
Reference


[52] KIM, EH. Understanding Effects of Silicon/Aluminum Ratio and Calcium Hydroxide on Chemical Composition, Nanostructure and Compressive Strength for Metakaolin Geopolymers. [Ph. D. Thesis]. University of Illinois at Urbana-Champaign; 2012.


Table 1. Chemical composition (weight %) of class F fly ash (FA) and waste concrete fines (WCF)

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>FA (%)</th>
<th>WCF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>58.9</td>
<td>57.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>26.5</td>
<td>6.57</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
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</tr>
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<td>CaO</td>
<td>4.20</td>
<td>17.5</td>
</tr>
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<td>MgO</td>
<td>1.15</td>
<td>1.71</td>
</tr>
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<td>SO$_2$</td>
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<tr>
<td>Na$_2$O</td>
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<td>4.53</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.09</td>
<td>1.68</td>
</tr>
</tbody>
</table>
Table 2. Two cement/aggregate ratios used in this research and the corresponding amount of cementitious materials and aggregates for one concrete specimen

<table>
<thead>
<tr>
<th>Cement/aggregate ratio&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Waste concrete fines (g)</th>
<th>Fly ash (g)</th>
<th>Coarse RA or NA (g)</th>
<th>Fine RA or sand (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.29</td>
<td>81.24</td>
<td>243.72</td>
<td>784.00</td>
<td>337.00</td>
</tr>
<tr>
<td>0.22</td>
<td>61.63</td>
<td>184.89</td>
<td>784.00</td>
<td>337.00</td>
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</tbody>
</table>

<sup>a</sup>: Cement = Waste concrete fines + Fly ash; and Aggregate = Coarse RA + Fine RA or NA + Sand. RA = recycled aggregate, NA = natural aggregate.
Table 3. Composition of geopolymer concrete (GPC) specimens prepared at different conditions.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Cement (g)</th>
<th>Aggregate (g)</th>
<th>Aggregate type</th>
<th>Water (g)</th>
<th>NaOH (g)</th>
<th>Na2SiO3 solution (g)</th>
<th>SS/N</th>
<th>W/C</th>
<th>C/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-22-05RA</td>
<td>246.52</td>
<td>1121.00</td>
<td>RA</td>
<td>40.39</td>
<td>18.49</td>
<td>117.76</td>
<td>2.00</td>
<td>0.46</td>
<td>0.22</td>
</tr>
<tr>
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<td>246.52</td>
<td>1121.00</td>
<td>RA</td>
<td>49.49</td>
<td>22.67</td>
<td>103.08</td>
<td>1.43</td>
<td>0.46</td>
<td>0.22</td>
</tr>
<tr>
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<td>91.64</td>
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<td>C/A</td>
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<td></td>
</tr>
</tbody>
</table>

Notes: RA = recycled aggregates, NA = natural aggregates, SS/N = Na₂SiO₃ solution/NaOH solution mass ratio, W/C = water to cement ratio, and C/A = cement to aggregate ratio. In specimen ID, the first 2 digits mean the NaOH concentration (10 or 14 M), the second 2 digits mean the cement/aggregate ratio (0.22 or 0.29), and the third 2 digits mean the NaOH solution/ Na₂SiO₃ solution mass ratio (0.5 to 1.3).
Table 4. Summary of NaOH concentrations and SS/N ratios for longest setting time from different geopolymer concrete research

<table>
<thead>
<tr>
<th>Geopolymer concrete research</th>
<th>Setting time range (min)</th>
<th>Optimum NaOH concentration, SS/N $^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>High calcium fly ash was used as binder to produce geopolymer concrete</td>
<td>28-68</td>
<td>15 M, 2.00</td>
<td>[25]</td>
</tr>
<tr>
<td>Ground granulated blast furnace slag (GGBFS) and ordinary Portland cement (OPC) were added into class F fly ash to produce geopolymer concrete</td>
<td>40-440</td>
<td>14 M, 1.50</td>
<td>[26-28]</td>
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<tr>
<td>Nano-SiO$_2$ and nano-$\text{Al}_2$O$_3$ were added into high calcium fly ash based geopolymer cement paste to study how different factors affect the setting time and mechanical properties</td>
<td>12-29</td>
<td>10 M, 2.00</td>
<td>[29]</td>
</tr>
<tr>
<td>Nano-silica was added into class F fly ash based geopolymer mortar at different NaOH concentrations</td>
<td>113-198</td>
<td>12 M, 1.75</td>
<td>[30]</td>
</tr>
<tr>
<td>High calcium fly ash was replaced by OPC at different dosages in geopolymer mortar</td>
<td>28-124</td>
<td>10 M, 0.67</td>
<td>[31]</td>
</tr>
<tr>
<td>High calcium fly ash based geopolymer paste at NaOH concentration from 8 to 18 M was studied</td>
<td>30-130</td>
<td>18 M, 0.67</td>
<td>[32]</td>
</tr>
<tr>
<td>Calcium chloride, calcium sulfate, sodium sulfate, and sucrose at different dosages were added into high calcium fly ash based geopolymer paste to study how different chemical admixtures affect the setting time and workability</td>
<td>26-90</td>
<td>10 M, 1.50</td>
<td>[33]</td>
</tr>
<tr>
<td>This study</td>
<td>21-151</td>
<td>10 M, 1.10</td>
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</tr>
</tbody>
</table>

$^a$: The NaOH concentration and SS/N ratio were the optimum values used by the researchers to acquire the longest setting time. SS/N = sodium silicate solution to NaOH solution mass ratio.
Table 5. Summary of NaOH concentrations and SS/N ratios for highest UCS from different geopolymer concrete research.

<table>
<thead>
<tr>
<th>Geopolymer concrete research</th>
<th>7 days UCS (MPa)</th>
<th>Optimum NaOH concentration, SS/N (^a)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>High calcium fly ash based geopolymer cement was used to produce geopolymer concrete. Specimens were cured at 60°C for the first 24 hours and then at room temperature (23°C).</td>
<td>19.9 - 41.2</td>
<td>20 M, 1.0</td>
<td>[25]</td>
</tr>
<tr>
<td>Ground granulated blast furnace slag (GGBFS) and ordinary Portland cement (OPC) were added to improve the strength of class F fly ash based geopolymer concrete. Specimens were cured at room temperature.</td>
<td>11.0 – 42.0</td>
<td>14 M, 2.5</td>
<td>[26-28]</td>
</tr>
<tr>
<td>Class F fly ash based geopolymer concrete was produced using NaOH concentration from 6 to 12M and SS/N ratio from 0.3 to 3. Specimens were cured at 60 °C for the first 24hrs and then at room temperature (23°C).</td>
<td>6.00 – 42.0</td>
<td>12 M, 1.0</td>
<td>[35]</td>
</tr>
<tr>
<td>Low calcium fly ash and bottom ash were used to produce geopolymer concrete. For comparison with OPC concrete, specimens were cured at ambient temperature.</td>
<td>0.20 - 12.6</td>
<td>14 M, 2.0</td>
<td>[36]</td>
</tr>
<tr>
<td>Class F fly ash based geopolymer concrete was produced at various NaOH concentrations, SS/N ratios, and aggregate to cement ratios. Specimens were first cured at temperature from 60 - 120°C for 6 – 72 hrs and then at room temperature. The highest 7-day UCS was obtained from the specimens cured 100 °C for 24 hrs.</td>
<td>13.0 – 58.0</td>
<td>10 M, 2.5</td>
<td>[37]</td>
</tr>
<tr>
<td>Class F fly ash based geopolymer concrete was produced by using a curing temperature of 60, 70, 80 and 90°C for 24 to 96 hrs and then curing at room temperature. The highest UCS was obtained from the specimens cured at 70 °C for 96hrs.</td>
<td>46.0 - 52.7</td>
<td>12 M, 2.5</td>
<td>[38]</td>
</tr>
<tr>
<td>This study</td>
<td>5.35 - 32.0</td>
<td>10 M, 1.1</td>
<td>(^a): The NaOH concentrations and SS/N ratios were the optimum values used by the researchers to acquire the highest UCS. SS/N = sodium silicate solution to NaOH solution mass ratio.</td>
</tr>
</tbody>
</table>
Fig. 1. Grain size distribution of class F fly ash (FA), waste concrete fines (WCF), and fine and coarse recycled aggregates (RA).
A: High calcium fly ash [25]
B: Class F fly ash and ground blast furnace slag [26]
C: Class F fly ash and ground blast furnace slag [27]
D: Class F fly ash and OPC [28]
E: High calcium fly ash, nano-SiO$_2$, nano-Al$_2$O$_3$ [29]
F: Class F fly ash [30]
G: High calcium fly ash, OPC [31]
H: High calcium fly ash [32]
I: High calcium fly ash, calcium chloride, calcium sulfate, sodium sulfate and sucrose [33]
J: High calcium fly ash, nano-silica, rice husk ash and nano alumina [28]
K: Class F fly ash [35]
L: Low calcium fly ash and bottom ash [36]
M: Class F fly ash, OPC [37]
N: Class F fly ash [38]
O: Current study

Fig. 2. NaOH concentrations used by different geopolymer concrete researchers.
Fig. 3. SS/N ratios used by different geopolymer concrete researchers.

A: High calcium fly ash [25]  B: Class F fly ash and ground blast furnace slag [26]
C: Class F fly ash and ground blast furnace slag [27]  D: Class F fly ash and OPC [28]
K: Class F fly ash [35]  L: Low calcium fly ash and bottom ash [36]
M: Class F fly ash, OPC [37]  N: Class F fly ash [38]
O: Current study
Fig. 4. Initial setting time of geopolymer concrete at different conditions. RA = recycled aggregates, NA = natural aggregates, and SS/N = Na$_2$SiO$_3$ solution/NaOH solution mass ratio. In specimen ID, the first 2 digits mean the NaOH concentration (10 or 14 M), the second 2 digits mean the cement/aggregate ratio (0.22 or 0.29), and the third 2 digits mean the water/cement ratio (0.46 or 0.40).
A: Class F fly ash-based geopolymer paste [30]
B: Class F fly ash and ground blast furnace slag-based geopolymer concrete [26]
C: Class F fly ash and ground blast furnace slag-based geopolymer concrete [27]
D: Class F fly ash and OPC-based geopolymer concrete [28]
E: High calcium fly ash, nano-SiO$_2$, nano-Al$_2$O$_3$-based geopolymer paste [29]
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J: High calcium fly ash, nano-silica, rice husk ash and nano alumina-based geopolymer paste [28]
K: Current research

Fig. 5. Initial setting time from different geopolymer concrete researchers.
Fig. 6. Comparison of coarse RA (left) and NA (right). RA = recycled aggregates, and NA = natural aggregates.
Fig. 7. UCS versus SS/N ($\text{Na}_2\text{SiO}_3$ solution/NaOH solution mass ratio) for GPC specimens cured at 35°C. In specimen ID, the first 2 digits mean the NaOH concentration (10 or 14 M), the second 2 digits mean the cement/aggregate ratio (0.22 or 0.29), H means the curing temperature of 35°C. RA = recycled aggregates, and NA = natural aggregates.
Fig. 8. UCS versus SS/N (Na$_2$SiO$_3$ solution/NaOH solution mass ratio) for GPC specimens cured at room temperature (23°C). In specimen ID, the first 2 digits mean the NaOH concentration (10 or 14 M), the second 2 digits mean the cement/aggregate ratio (0.22 or 0.29), R means the curing temperature is room temperature (23°C). RA = recycled aggregates, NA = natural aggregates.
<table>
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<tr>
<th></th>
<th>Description</th>
<th>Reference</th>
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<tbody>
<tr>
<td>A</td>
<td>Class F fly ash-based concrete [38]</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Class F fly ash and ground blast furnace slag-based geopolymer concrete [26]</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Class F fly ash and ground blast furnace slag-based geopolymer concrete [27]</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Class F fly ash and OPC-based geopolymer concrete [28]</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Class F fly ash-based geopolymer mortar [35]</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Low calcium fly ash and bottom ash-based geopolymer concrete [36]</td>
<td></td>
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<tr>
<td>G</td>
<td>Class F fly ash and OPC-based geopolymer concrete [31]</td>
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<td>I</td>
<td>Current research</td>
<td></td>
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</table>

Fig. 9. UCS of GPC from different geopolymer concrete researchers.
Fig. 10. Comparison of UCS of GPC specimens produced from RA and NA at SS/N = 1.1 and NaOH concentration = 10 M. In the figure, H means the curing temperature of 35°C, R means the room curing temperature of 23°C, RA = recycled aggregates, NA = natural aggregates, and SS/N = Na₂SiO₃ solution/NaOH solution mass ratio.
Fig. 11. The interfacial transition zone in geopolymer concrete produced from recycled aggregates (RA) (left) and that from natural aggregates (NA) (right). A: The new interfacial transition zones between NA and geopolymer cementitious material.
APPENDIX D

UTILIZATION OF ALUMINUM SLUDGE (AS) TO ENHANCE MINE TAILINGS-BASED GEOPOLYMER

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Abstract

This paper investigates the feasibility of using aluminum sludge (AS) to enhance copper mine tailings (MT)-based geopolymer. The Si/Al and Na/Al molar ratios were adjusted by adding AS into the high silica content MT and using different amount of NaOH. Unconfined compression tests and SEM, XRD and FTIR studies were conducted on geopolymer specimens prepared at different Si/Al and Na/Al ratios and after 7 day curing. The results indicate that by adding AS and utilizing appropriate amount of NaOH, the unconfined compressive strength (UCS) increases significantly. The main reason is because the addition of AS along with utilization of appropriate amount of NaOH makes both the Si/Al and Na/Al ratios reach the optimum values for geopolymerization, leading to higher degree of geopolymerization and more compact geopolymer microstructure. Based on this study, it can be concluded that AS can be used to effectively enhance the MT-based geopolymer.

Key words: Geopolymer; Aluminum sludge; Mine tailings; Unconfined compressive strength; Microstructure.
1. Introduction

Mine tailings (MT) are fine materials, primarily ground rock, left over after extraction of valuable minerals from ore [1]. A very approximate estimate indicates that more than seven billion tonnes of MT are generated by worldwide mining industry every year [2]. Copper MT primarily consist of rock forming minerals, but may also contain sulfide minerals. The disposal of MT not only occupies large areas of land but also poses a threat to the environment [3].

Researchers have been working on the recycling and utilization of MT to produce construction materials, which not only addresses the environmental concerns related to MT disposal but also saves the land and costs required for MT disposal. Sultan [4,5] studied the feasibility of applying copper MT to highway construction by investigating the engineering properties of untreated, cement-stabilized and asphalt-stabilized MT and concluded that copper MT have excellent engineering properties and can be easily adapted for use in road construction. Teredesai [6] conducted laboratory experiments to assess the potential of MT abandoned from mines as roadway base material. The tailings were stabilized with 10% class C fly ash (CFA) and 10% cement kiln dust (CKD) respectively. The results indicated that the unconfined compressive strength and elastic modulus were enhanced significantly due to the utilization of CFA and CKD. Based on the literature review, so far the research on stabilization of MT is still limited and focuses on the stabilization using cement, lime or material containing sufficient amount of calcium. However, the products from the reaction with calcium have several limitations such as low acid resistance, poor immobilization of heavy metals, and high energy usage and greenhouse gas emissions related to the ordinary Portland cement (OPC) [7].

During the past decades, the geopolymerization technology proposed by Davidovits [8] has attracted great interest of researchers from both material and civil engineering fields.
Geopolymerization is the reaction of aluminosilicates with an alkaline hydroxide or silicate solution to generate an amorphous cementitious material called geopolymer. Geopolymer has a polymeric structure with three dimensional (3D) interconnected -Si-O-Al-O-Si- bonds and shows many advantages over OPC such as rapid mechanics strength development, high resistance to acid, efficient immobilization of heavy metal and hazardous chemicals, and reduced energy consumption and greenhouse gas emissions [9-13]. Since MT are fine in particle size and contain a large amount of silica and alumina components, they are a potential source material for geopolymer production. Zhang and his research group [14-18] conducted systematic study on geopolymerization of copper MT so that they can be used as construction material in an environmentally-friendly way. The results indicate that by properly selecting the preparation conditions (initial water content, NaOH concentration, forming pressure and curing temperature), the copper MT generated in Arizona can be used to produce bricks meeting the ASTM requirements on strength, water absorption, and abrasion resistance for nearly all types of applications.

Research results show that the formation of geopolymer is affected not only by the curing condition such as temperature, humidity and time but also by the Si/Al and Na/Al molar ratios of the source material(s) [13,18-33]. For example, in the investigation by Zhang et al. [18], the Si/Al ratio of copper MT was adjusted by adding class F fly ash and the highest strength of the MT-based geopolymer specimens was obtained at a Si/Al ratio equal to 1.89. Xu and Van Deventer [19] used different combinations of albite, fly ash and kaolinite to study the effect of Si/Al ratio on the UCS of geopolymer specimens. The highest UCS of 45 MPa was obtained at a Si/Al ratio of 2 for specimens cured at 40°C for 7 days. Besides the Si/Al ratio, researchers also studied the effect of Na/Al ratio on the mechanical properties of geopolymer. For example, according to Kani and
Allahverdi [20], the concentration of NaOH solution and thus the Na/Al ratio has great effect on the strength of produced geopolymer specimens. They concluded that the optimum Na/Al ratio (or the Na/Al ratio at the highest compressive strength) is 0.92.

Since the Si/Al and Na/Al ratios are so vital to the production of geopolymer, this paper investigates the effect of Si/Al and Na/Al ratios on the properties of MT-based geopolymer. By adding different amount of aluminum sludge (AS) (which is a potential water treatment residual product from mining)) into the high silica content MT and utilizing appropriate amount of NaOH, the Si/Al and Na/Al ratios were adjusted. The UCS and water loss of geopolymer specimens prepared at different Si/Al and Na/Al ratios and after 7 day curing were measured. To better understand the mechanism behind the improvement of the properties of MT-based geopolymer, SEM, FTIR and XRD analyses were also performed.

2. Experiment study

2.1. Materials

The materials used in this investigation include copper mine tailings (MT), aluminum sludge (AS), reagent grade 98% sodium hydroxide (NaOH), and de-ionized water. Both the MT and AS were supplied by the Sierrita Mine Operations of Freeport-McMoRan Copper & Gold Inc. in Tucson, Arizona. The MT were received in the form of damp solids and the AS in the form of dried filter cake aggregate. The MT were directly used as received after drying but the AS was crushed and milled to powder before used. Table 1 shows the main chemical composition of the MT and AS based on XRF analysis. The MT mainly contains silica and aluminum with substantial amount of calcium and potassium, while the AS contains mainly aluminum with substantial amount of sulfur and sodium, which allows the Si/Al ratio to be easily adjusted by adding different amount of AS into the MT. Following ASTM D6913 and D422, the particle size distribution was determined for
both the MT and AS powders screened using mesh No. 60 (250 \( \mu \)m) sieve and used for producing the geopolymer samples (see Fig. 1). The MT and AS have about the same mean particle size but the MT have more fine particles than the AS. The SEM micrographs of the MT and AS powders are shown in Fig. 2. The MT and AS both have irregular particle shapes but the MT have more fine particles attached to the surface of coarse particles. Fig. 3 shows the XRD patterns of the MT and AS powders. The MT are mainly crystalline materials consisting of quartz (SiO\(_2\)) and albite (NaAlSi\(_3\)O\(_8\)). A weak amorphous phase, centered around 28°, can also be seen from the XRD pattern. The amorphous phase is the main reactive phase for geopolymerization but, as seen in [15], the crystalline phase also participates in the geopolymerization process. For the AS, the XRD pattern is much more amorphous due to the solution precipitation process used to produce the AS, and the main crystalline phases are mullite, quartz and some sodium aluminum silicate hydrate.

The NaOH flakes were purchased from Alfa Aesar Company in Ward Hill, Massachusetts. The NaOH solution is prepared by dissolving the NaOH flakes in de-ionized water.

2.2. Sample preparation and test methods

Three AS contents, 0%, 10% and 20 wt.% (by total solid weight), were designed to adjust the Si/Al ratio of the source material. Simultaneously, the NaOH/total solid weight ratio was changed to adjust the Na/Al ratio in the range from 0.8 to 1.3. To produce geopolymer specimens, the dry AS powder was first thoroughly mixed with the dry MT powder at a specified AS content. Then the NaOH solution was slowly added into the mixture while mixing. Since the addition of AS resulted in higher workability for the paste, the amount of water used for sample preparation was adjusted accordingly (see Table 2) to ensure the same workability for all pastes. The resulted paste was poured into the Harvard miniature compaction cylindrical molds of 33.4 mm diameter and 72.5 mm height with minor compaction. The prepared specimens were then pressed under a 0.5 MPa
forming pressure at the top for 1 minute. After the compression, the specimens were de-molded, weighed and then placed in an oven for curing at 90 °C for 7 days before tested. The curing temperature was selected based on the previous studies [14-18].

After the curing, the specimens were weighed again so that the water loss during the curing process could be determined. Then unconfined compression tests were performed on the specimens with an ELE Tri Flex 2 loading machine at a constant loading rate of 0.1 mm/min. The tests were performed to measure the UCS of the specimens produced at different conditions. For each condition, considering the relatively small variance of measurements, three specimens were tested and the average of the measured values was used. Before conducting the compression test, the end surfaces of the specimens were polished to make sure they are accurately flat and parallel. In addition, the end surfaces were lubricated to minimize the friction between the specimen and the steel platens.

SEM, XRD and FTIR analyses were also performed to investigate the microstructure and phase composition of the MT-based geopolymer specimens containing different amount of AS. The SEM imaging was performed in SE conventional mode using the FEI INSPEC-S50/Thermo-Fisher Noran 6 microscope. The XRD analysis was performed with a Scintag XDS 2000 PTS diffractometer using Cu Kα radiation, at 2.00 degree/min ranging from 10.00° to 70.00° with 0.600 s count time. The Thermo Nicolet 370 FTIR/EZ Omnic with a smart performance ATR ZnSe crystal was used to conduct the FTIR analysis. The wavelengths ranged from 600 to 4000 cm⁻¹.

Table 2 summarizes the combination of variables studied and the different types of tests performed.

3. Results and discussion

3.1. Macro-scale properties
Fig. 4 shows the variation of UCS with Na/Al ratio at different AS contents. The UCS increases with the Na/Al ratio until Na/Al = 1.1 and then starts to decrease substantially with higher Na/Al, giving an optimum Na/Al ratio of 1.1. By adding more AS, the UCS increases substantially, especially when the Na/Al ratio is greater than 1.0. At the optimum Na/Al ratio of 1.1, the UCS values at 10% and 20% AS are respectively 22.3 and 56.9% higher than that at 0% AS.

By adding 10% and 20% AS, the Si/Al ratio was decreased from 3.38 of the pure MT to 2.71 and 2.17, respectively. It can be seen from Fig. 4 that the UCS increases at all Na/Al ratios when the Si/Al ratio decreases from 3.38 to 2.71 and 2.17.

It is known that the geopolymerization process can be divided into three essential steps: dissolution of aluminosilicates by alkali to produce small reactive silica and alumina species; reorientation (transportation) of dissolved species into monomers; and polycondensation to form amorphous or semi-crystalline aluminosilicate polymers. According to Xu and Van Deventer [19], the formation of geopolymer can be schematically illustrated by the following two reactions:

\[
\begin{align*}
\text{n(Si}_2\text{O}_3\text{Al}_2\text{O}_5) + 2\text{nSiO}_2 + 4\text{nH}_2\text{O} + \text{NaOH} & \rightarrow \text{Na}^+ + \text{n(OH)}_2\text{-Si-O-Al-O-Si-(OH)}_2^- \\
(\text{Si-Al material}) & \quad (\text{Geopolymer precursor}) \\
\text{n(OH)}_2\text{-Si-O-Al-O-Si-(OH)}_2^- + \text{NaOH} & \rightarrow \text{Na}^+ \text{-(Si-O-Al-O-Si-O-)}_{2n+1} + 4\text{nH}_2\text{O} \\
(\text{Geopolymer precursor}) & \quad (\text{Geopolymer backbone})
\end{align*}
\]

It is can be seen from the above two reactions that the amount of silica and alumina in the raw material and the content of NaOH play a vital role in the formation of the final geopolymer product. This is probably why much research has been conducted to study the effect of Si/Al and Na/Al ratios on geopolymerization [13,18-33]. The reported research results indicate that in order to obtain a geopolymer with maximum strength, the Si/Al ratio in general should be in the range of
1 to 3, the specific value dependent on the source material used. Duxson et al. [13] studied the effect of Si/Al ratio on the microstructure and mechanical properties of metakaolin based geopolymer and found that 1.9 is the ratio corresponding to the maximum compressive strength. Zhang et al. [18] studied the geopolymer produced from mixed copper mine tailings and fly ash and obtained the highest compressive strength at Si/Al = 1.89. Cheng and Chiu [21] reported that a Si/Al ratio of 1.58-1.73 results in the highest strength values for the geopolymer produced from mixed metakaolin and blast furnace slags. Stevenson and Sagoe-Crentsil [22,23] reported the optimum Si/Al ratio of 1.75-1.9 and 1.95 for metakaolin and fly ash based geopolymers, respectively. De Silva et al. [24] reported that the highest 3 day compressive strength for metakaolin based geopolymer is at a Si/Al ratio of 1.9. Zheng et al. [25] showed that a Si/Al ratio close to 2.0 is the optimum one for municipal solid waste incinerator (MSWI) fly ash based geopolymer. Rowles and O’Connor [26,27] studied the geopolymer produced from metakaolin and sodium silicate solution prepared with sodium hydroxide and silica fume and found that the maximum compressive strength was obtained at a Si/Al ratio about 2.5. Xu and Van Deventer [28] tested different combinations of kaolinite, albite and fly ash and showed that the geopolymers synthesized with the mixture of all three materials and the mixture of kaolinite and fly ash reach the highest compressive strength at a Si/Al ratio respectively of 2.1 and 2.0. Perera et al. [29] reported that the most compact metakaolinite-based geopolymer specimen was obtained at a Si/Al ratio of 2.0. Zhang et al. [30] studied the effect of Si/Al ratio on the compressive strength of metakaolin-based geopolymer and obtained the highest compressive strength at Si/Al = 2.75. Liew et al. [31] and Heah et al. [32] also conducted research on metakaolin-based geopolymer but the highest compressive strength was obtained at respectively Si/Al = 1.55 and 1.64. Fig. 5(a) summarizes the optimum Si/Al values obtained by the different researchers. The Si/Al ratio of
2.17 at 20% AS used in the current study just falls in the range of the reported optimum Si/Al values.

The effect of Na/Al ratio on geopolymerization can be explained by the two roles of NaOH solution in geopolymerization, dissolution of silica and alumina species and charge-balancing of alumina species by providing metal cations. The increase in UCS with higher NaOH content (or greater Na/Al ratio) is mainly due to the dissolution of more silica and alumina components and thus incorporation of larger quantities of silica and alumina components in geopolymerization [33-35]. However, this effect is true only up to a certain level, after which the increase in NaOH content results in no increases or in most cases decrease of strength, possibly due to the presence of excess Na ions in the geopolymer framework [34,36,37]. Panagiotopoulou et al. [37] showed that silica leaching in NaOH solution for different source materials increases up to 10 M and further increase in the alkalinity does not lead to more dissolution of silica. Stevenson and Sagoe-Crentsil [22,23] studied metakaolin and fly ash based geopolymers and reported the same optimum Na/Al ratio of 1.0 for both of them. De Silva et al. [24] reported that the highest 3 day compressive strength for metakaolin based geopolymer is at a Na/Al ratio of 1.0. Rowles and O’Connor [26,27] reported that the geopolymer produced by sodium silicate activation of metakaolin reached the highest compressive strength at a Na/Al ratio of 1.30. Perera et al. [29] reported that they obtained the most compact metakaolinite-based geopolymer specimens at a Na/Al ratio of 1.0. Zhang et al. [30] studied the effect of Na/Al ratio on the compressive strength of calcined kaolin-based geopolymer and found that the highest compressive strength is at Na/Al = 1.0. Liew et al. [31] studied kaolin-based geopolymer and obtained the highest compressive strength at Na/Al = 1.15. Heah et al. [32] also conducted research on kaolin-based geopolymer but obtained the highest compressive
strength at Na/Al = 1.09. Fig. 5(b) compares the optimum Na/Al ratio of 1.1 from the current study with those by the different researchers and a good agreement can be easily seen.

It is noted that the optimum Si/Al and Na/Al ratios are related to each other because they both affect the geopolymerization process. The highest compressive strength may not be obtained when only one of them is at the optimum value. Fig. 6 summarizes the optimum Si/Al and Na/Al ratios in the same figure reported by the researchers described in the previous two paragraphs. The Si/Al and Na/Al ratios, 2.17 and 1.1, at 20% AS used in the current study just fall in the middle of the reported values.

After the curing and before the UCS test, the specimens were also weighed in order to determine the amount of water loss during the curing process. In this paper, the water loss ratio, $L$, as defined below, is used to show the level of water loss during the curing process:

$$L = \frac{W_1 - W_2}{W_w} = \frac{W_1 - W_2}{\frac{w}{1+w}W_1}$$  \hspace{1cm} (3)

where $W_1$ is the initial weight of a specimen before curing; $W_2$ is the weight of the specimen after curing and before UCS test; $W_w$ is the initial weight of water in the specimen before curing; and $w$ is the water to solid weight ratio used in the preparation of the specimen (see Table 2).

Fig. 7 shows the water loss ratio versus Na/Al ratio at different AS contents. To better show the effect of water loss during curing on the UCS, the variation of UCS with Na/Al ratio at different AS contents is also included in this figure. As shown in equations (1) and (2), water is released during the geopolymerization process. So the water loss ratio indirectly indicates the degree of geopolymerization at the same curing conditions. It can be seen from the figure that when Na/Al > 1.1, the water loss ratio decreases significantly with higher Na/Al ratio at both 0% and 10% AS contents. This is mainly because the rate of condensation between silicate species themselves is
slower than that between aluminate and silicate species [38-41]. Due to the high Si/Al ratios, 3.38 and 2.71 at respectively 0% and 10% AS, and the large amount of NaOH at high Na/Al ratio > 1.1, the dissolved Si is much more than the dissolved Al. The extra dissolved Si species tend to condense between themselves and thus the overall geopolymerization reaction speed is slowed and the loss of water after 7 days’ curing is decreased.

Based on the above analysis, it can be concluded the copper MT has sufficient amount of Si required for synthesis of geopolymer. By adding AS to the MT and utilizing appropriate amount of NaOH, the Si/Al and Na/Al ratios can be both adjusted to be closer to the optimum values, leading to higher degree of geopolymerization and thus greater UCS of the produced geopolymer. This will be further discussed based on the SEM. FTIR and XRD results presented in next section.

3.2. Micro/nano-scale properties

The SEM micrographs of geopolymer samples at the same Na/Al ratio of 1.1 and three different Si/Al ratios (AS contents), 3.38 (0%), 2.71 (10%) and 2.17 (20%), are compared in Fig. 8. Two distinct phases can be found in all three pictures, which are the sponge-like geopolymer gels and the unreacted or partially reacted particles denoted by “G” and “U”, respectively. More geopolymer gels can be seen at higher AS contents, indicating that higher degree of geopolymerization has occurred. This is also reflected by the decrease of the number of unreacted particles at higher AS contents. At 20% AS content, essentially no unreacted particles can be seen. A large void and several small voids can be seen in the 0% and 10% AS samples respectively. For the 20% AS sample, the geopolymer gels almost completely fill all voids. The larger amount of geopolymer gels and the more compact microstructure lead to the increase of UCS at higher AS contents as described in the previous section.
Fig. 9 shows the SEM micrographs of the same three samples at a higher magnification. Some unreacted NaOH (or newly formed Na$_2$CO$_3$) donated by “S” can be easily seen in the 0% AS sample (Fig. 9a) but not in the 10% (Fig. 9b) or 20% (Fig. 9c) AS sample. Since the three samples had the same Na/Al ratio of 1.1, the 0% AS sample contained the smallest amount of Al and thus the smallest amount of NaOH. Although less NaOH was used in the 0% AS sample than in the 10% and 20% AS samples, the shortage of the more amorphous Al from AS hindered the geopolymerization process and thus some NaOH did not participate in chemical reaction and remained on the surface of geopolymer gels and unreacted particles after curing. The lower degree of geopolymerization reaction of the 0% AS sample is also reflected by the much smaller amount of amorphous sponge-like geopolymer gels in it (Fig. 9a) than in the 10% and 20% AS samples (Figs. 9b and 9c). This further demonstrates the improvement of geopolymerization after AS is added to the copper MT to adjust the Si/Al ratio to be closer to the optimum value.

Fig. 10 shows the IR spectra of the MT powder, the AS powder and the geopolymer specimens prepared at Na/Al = 1.1 and with respectively 0%, 10% and 20% AS. The identified IR characteristics are summarized in Table 3. The spectra of the MT powder exhibit a primary band at around 1000 cm$^{-1}$ and several satellite bands over 800-1200 cm$^{-1}$. The principal band corresponds to the asymmetric stretching vibrations of Si-O-Si or Al-O-Si [43]. Some researchers used SiQ$^n$(mAl) units to describe the structural units in aluminosilicates, where $n$ and $m$ represent the extent of Si and Al involved in the geopolymerization process. The FTIR active stretching vibration of Si-O in SiQ$^n$ units centered around 1200, 1100, 950, 900 and 850 cm$^{-1}$ when $n = 4, 3, 2, 1$ and 0 respectively. The small band centered at 2350 cm$^{-1}$ is attributed to the vibration of C-O from CO$_2$ trapped in the specimen. In the spectra of the AS powder, the intense peak at 1100 cm$^{-1}$ can be assigned to the asymmetric stretching vibration of Si-O. There are also two wider and
weaker peaks over 1600-1700 cm\(^{-1}\) and 3200-3500 cm\(^{-1}\) which can be assigned to the stretching vibration of O-H indicating that the AS powder may have absorbed some water in air [45,46]. The absorbed water may be the reason why the AS powder has no band at 2350 cm\(^{-1}\) attributed to the vibration of C-O from CO\(_2\). After geopolymerization, the primary band of MT shifted to lower wavenumbers since more Al takes place of Si within the geopolymer chains and the energy of Al-O is weaker than that of Si-O [47]. The principal bands for the three geopolymer specimens are intense but lack a sharp feature indicating that the geopolymer molecular chains are amorphous. Another evident new band for the geopolymer specimens is located around 1450 cm\(^{-1}\) and attributed to the stretching of C-O-C from CO\(_3^{2-}\) [49]. Because of the CaO in the MT (and also in the AS), two types of carbonates, CaCO\(_3\) and Na\(_2\)CO\(_3\), can be generated during the specimen preparation process. Before involved in geopolymerization, some of the CaO may react with CO\(_2\) from the air and water in both the alkaline solution and the moist atmosphere to generate CaCO\(_3\) [50]. Analogously some Na\(_2\)CO\(_3\) can also be generated simultaneously [51]. The band centered at 2350 cm\(^{-1}\) retains because there is still CO\(_2\) that is trapped in the geopolymer specimens. Finally the weak band that centers around 3400 cm\(^{-1}\) can still be seen for the 0% AS sample but not for the 10% and 20% AS samples. Since this band corresponds to the O-H stretching vibration related to water, it indicates that the water in the 0% AS samples is not completely expelled out or the geopolymerization is not complete, confirming the results presented earlier.

Fig. 11 shows the XRD patterns of the source materials and the geopolymer specimens produced at Na/Al = 1.1 and with respectively 0%, 10% and 20% AS. After geopolymerization, no significant new peaks appear, indicating that the geopolymerization process did not generate substantial amount of new crystalline materials. Some of the albites appearing in the pattern of MT powder turn into sodium aluminum silicate hydrates in the patterns of 0% and 10% AS geopolymer
specimens but remains as albites in the pattern of the 20% AS geopolymer specimen. As shown in equations (1) and (2) and stated earlier, the geopolymerization process releases extra water. The released water can be quickly evaporated into air during the curing at 90 °C. As shown in Fig. 7, the 20% AS geopolymer specimen lost the most amount of water during curing. The lack of water prevents the formation of sodium aluminum silicate hydrate. On the other hand, more water was trapped within the 0% and 10% AS specimens, allowing the formation of sodium aluminum silicate hydrate. So the XRD results further confirm the results described earlier.

4. Conclusions

This paper presents the results of a feasibility study on utilization of AS to enhance copper MT-based geopolymer. Based on the investigation, the following conclusions can be drawn:

1) By adding AS into MT and utilizing appropriate amount of NaOH, the Si/Al and Na/Al ratios can be adjusted to be closer to the optimum values and the physical and mechanical properties of the MT-based geopolymer can be improved significantly. By adding 10% and 20% AS to MT, the Si/Al ratio is decreased from 3.38 to respectively 2.71 and 2.17 and the UCS at the optimum Na/Al ratio of 1.1 is increased from 28.5 MPa to respectively 34.9 and 44.8 MPa.

2) The enhancement of the MT-based geopolymer with the addition of AS can be attributed to the following reasons:
   - Addition of AS to MT decreases the Si/Al ratio of the high silica content MT, leading to appropriate relative amount of Si and Al and thus enhancing the degree of geopolymerization.
• Addition of AS to MT increases the speed of geopolymerization because more condensation will be between the Si and Al species than between the Si species themselves due to the more amorphous alumina from the AS.

Acknowledgement

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References


Table 1. Chemical composition (weight %) of aluminum waste (AS) and copper mine tailings (MT).

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<tr>
<th>Chemical Compound</th>
<th>AS (%)</th>
<th>MT (%)</th>
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Table 2. Combination of variables studied and different types of tests conducted in this investigation.

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Table 3. FTIR absorption bands identified in AS and MT powders and geopolymer specimens shown in Fig. 10.

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Fig. 1. Particle size distribution of MT and AS powders.
Fig. 2. SEM micrographs of AS and MT powders.
Fig. 3. XRD pattern of AS and MT powders [A: albite, H\textsubscript{1}: Mordenite (Na), M: mullite, P: sanidine, S: quartz]
Fig. 4. UCS versus Na/Al ratio at different AS contents (Si/Al ratios).
Fig. 5. Optimum Si/Al and Na/Al ratios from different researchers.

(a) Optimum Si/Al Ratio

A: Metakaolin [13];
B: Copper mine tailings and fly ash [18];
C: Metakaolin and blast furnace slag [21];
D: Metakaolin [22];
E: Fly ash [23];
F: Metakaolin [24];
G: Municipal solid waste incinerator fly ash [25];
H: Metakaolin [26,27];
I: Kaolinite and fly ash [28];
J: Kaolinite, albite and fly ash [28];
K: Metakaolin [29];
L: Metakaolin [30];
M: Metakaolin [31];
N: Metakaolin [32];
O: Copper mine tailings and aluminum sludge (current research)

(b) Optimum Na/Al Ratio

D: Metakaolin [22];
E: Fly ash [23];
F: Metakaolin [24];
H: Metakaolin [26,27];
K: Metakaolin [29];
L: Metakaolin [30];
M: Metakaolin [31];
N: Metakaolin [32];
O: Copper mine tailings and aluminum sludge (current research)
Fig. 6. Optimum Si/Al and Na/Al ratios from different researchers presented in the same figure.
Fig. 7. Relationship between water loss ratio ($L$) and UCS.
Fig. 8. SEM micrographs of samples at constant Na/Al = 1.1, with different Si/Al ratios and cured at 90°C for 7 days: (a) 0% AS, (b) 10% AS, and (c) 20% AS. G and U denote geopolymer gels and unreacted or partially reacted particles respectively.
Fig. 9. Higher magnification SEM micrographs of samples at constant Na/Al ratio =1.1, with different AS contents and cured at 90°C for 7 days: (a) 0% AS, (b) 10% AS, and (c) 20% AS. S denotes sodium hydroxide.
Fig. 10. FTIR spectra of AS powder, MT powder and geopolymer specimens containing different amount of AS.
Fig. 11. XRD pattern of geopolymer specimens containing different amount of AS [A: albite, H₁: Mordenite (Na), H₂: 1.06Na₂OAl₂O₃·1.60SiO₂·1.60H₂O, M: mullite, P: sanidine, S: quartz].
APPENDIX E

MOLECULAR DYNAMICS STUDY OF SODIUM ALUMINOSILICATE GEOPOLYMER CONTAINING CALCIUM

Paper was prepared to submit to a journal

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Abstract

Molecular dynamics (MD) simulations were performed to study the effect of calcium content on the microstructure and mechanical properties of sodium aluminosilicate geopolymer. The sodium in the geopolymer system was replaced by calcium at 25, 50, 75 and 100%, respectively. Uniaxial compression tests were conducted through the MD simulation, and the results were compared with those from macro-scale physical experiments. The results show that by increasing the calcium content, the strength of the whole geopolymer system was improved. This trend agrees with the macro-scale experiment results indicating that by adding high-calcium content source materials, the strength of geopolymer products can be improved effectively. The results of this study provide useful information for predicting the changing trend of the mechanical properties when calcium content is adjusted in the geopolymer system.

Key words: Geopolymer, molecular dynamics, calcium content, mechanical properties
1. Introduction

Concrete has been widely used as a construction material for a long time. Ordinary Portland cement (OPC) is commonly used as the concrete binder. However, producing 1 ton of OPC needs to consume 1.5 tons of resource material and releases 0.9 ton of greenhouse gases [1]. The growing awareness of sustainability and climate change issues has been pushing the construction industry to look for alternative materials [2-4].

In recent years, researchers have been working on a new technology called geopolymerization, considering the advantages of low energy consumption and excellent mechanics properties of geopolymer. Geopolymer is a synthetic aluminosilicate material produced by using high concentration alkaline solution to dissolve silicates and aluminates from solid aluminosilicate source materials. The source materials of aluminosilicate can be different types of industrial wastes such as mine tailings, fly ash, cement kiln dust, and aluminum sludge. Researchers have developed the application of geopolymerization technology to produce geopolymer bricks and concrete from waste materials [5-9]. Ahmari et al. [10] used waste concrete fines together with class F fly ash to produce geopolymer paste. It is found that that Ca enhances the strength of geopolymer, supporting the results from other researchers [11-14].

It is noted that the research on geopolymer so far has been mainly focusing on experimental studies. Although much has been learnt from the experimental investigations, the underlying mechanisms at nano-scale behind the unique properties of geopolymer are still not fully understood. As research continues, to better understand and design geopolymer, more focus needs to be put on studying the underlying atomic-scale mechanisms using new tools such as molecular dynamics (MD) simulations.
MD can be an efficient tool to investigate the thermodynamic and kinetic properties of a particular material at the molecular level [15]. It has the advantage of being able to adjust the micro-structure of a particular material to quantify the chemical and physical mechanism. In the MD simulations, the interatomic potential that describes the interaction between atoms and molecules plays the most important role. Based on the experience from physical experiments and the first-principles theory, the interatomic potential is designed to not only replicate the thermodynamics properties but also determine the mechanical response to the external stimulus of certain materials [16-18]. As a result, MD is not only a complementary source to physical experimentation but also gives a way to verify the explanation of the physical experiment phenomena. In this way, it requires physical experiment and MD simulation work corporately to acquire a comprehensive view of a particular material. Since MD is an effective tool, many researchers used it to study cementitious materials. For example, Faucon et al. [19] used MD simulation to understand the breaking mechanisms of the calcium silicate hydrate chain with different Ca/Si ratios. Dai and Hu [20] used MD simulation to study cement hydration products and obtained results similar to those from experimental X-ray diffraction. Murray et al. [21] predicted the tensile and compressive strength by simulating the calcium silicate hydrate gel using the MD method. Sperinck et al. [22] studied the process of dihydroxylation of kaolinite to metakaolin and simulated this process successfully through the MD technology. Sadat et al. [23] used the MD simulation to investigate the structure and mechanical properties of sodium aluminosilicate geopolymers. The optimum Si/Al molar ratio obtained from their simulations is in good agreement with the physical experimental results.

In this paper, the molecular model of sodium aluminosilicate geopolymer built by Sadat et al. [23] was used to study the effect of calcium on the behavior of geopolymer by replacing the sodium atoms in the model with different amount of calcium. Uniaxial compression tests were conducted
in the MD simulations to predict the change of mechanical properties when different amount of Na was replaced by Ca. By comparing the simulation results with the macro-scale experimental results from Ahmari et al. [10], the validity of the molecular model was examined.

2. Simulation procedure

The force field used in this research is condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS). This force field enables accurate and simultaneous prediction for both organic and inorganic polymer systems [24, 25]. The atomic potential of COMPASS force field includes valence and non-bond interactions. The functions used in COMPASS force field can be calculated as below [25]:

\[
E_{\text{pot}} = \sum_b [K_2(b - b_0)^2 + K_3(b - b_0)^3 + K_4(b - b_0)^4] \\
+ \sum_\theta [H_2(\theta - \theta_0)^2 + H_3(\theta - \theta_0)^3 + H_4(\theta - \theta_0)^4] \\
+ \sum_\varphi [V_1(1 - \cos \varphi) + V_2(1 - \cos 2\varphi) + V_3(1 - \cos 3\varphi)] + \sum_\chi K_\chi \chi^2 \\
+ \sum_{b,b'} F_{b,b'}(b - b_0)(b' - b_0') + \sum_{\theta, \theta'} F_{\theta, \theta'}(\theta - \theta_0)(\theta' - \theta'_0) \\
+ \sum_{b, \theta} F_{b, \theta}(b - b_0)(\theta - \theta_0) + \sum_{b, \varphi} (b - b_0)(V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi) \\
+ \sum_{b', \varphi} (b' - b'_0)(V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi) \\
+ \sum_{\theta, \varphi} (\theta - \theta_0)(V_1 \cos \varphi + V_2 \cos 2\varphi + V_3 \cos 3\varphi) \\
+ \sum_{\varphi, \theta, \theta'} K_{\varphi, \theta, \theta'} \cos \varphi(\theta - \theta_0)(\theta' - \theta'_0) + \sum_{l, j} q_i q_j \\
+ \sum_{l, j} \epsilon_{l, j} \left[ 2 \left( \frac{r_{l, j}^0}{r_{l, j}} \right)^9 - 3 \left( \frac{r_{l, j}^0}{r_{l, j}} \right)^6 \right] \\
\] (1)
\( E_{\text{pot}} \) Potential energy  \( \chi \) Out-of-plane angle

\( K_2, K_3, K_4 \) Bond coefficients  \( F_{b,b}' \) Bond-bond coefficient

\( b, b' \) Bond lengths  \( F_{\theta,\theta}' \) Angle-angle coefficient

\( b_0, b_0' \) Equilibrium bond strength  \( F_{b,\theta} \) Bond-angle coefficient

\( H_2, H_3, H_4 \) Angle coefficients  \( K_{\phi,\theta,\theta}' \) Dihedral-angle-angle coefficient

\( \theta, \theta' \) Angles  \( q_i, q_j \) Charge

\( \theta_0, \theta_0' \) Equilibrium angles  \( \epsilon \) Dielectric constant

\( V_1, V_2, V_3 \) Dihedral coefficients  \( r_{ij} \) Distance

\( \phi \) torsion angle  \( K_7 \) Improper coefficient

\( \epsilon \) and \( r^0 \) are given for like atom pairs. The unlike atom pairs can be calculated following the 6th order combination law as below [26]:

\[
\eta_{ij}^0 = \left( \frac{(r_{ij}^0)^6 + (r_{ij}'^0)^6}{2} \right)^{\frac{1}{6}}
\]

(2)

\[
\epsilon_{i,j} = 2\sqrt{\epsilon_i \cdot \epsilon_j} \left( \frac{(r_{ij}^0)^3 (r_{ij}'^0)^3}{(r_{ij}^0)^6 (r_{ij}'^0)^6} \right)
\]

(3)

The partial atomic charge model is used to describe the electrostatic interaction. The net partial charge of an atom \( q_i \) can be calculated as follows:

\[
q_i = \Sigma_i \delta_{i,j}
\]

(4)

where \( \delta_{i,j} \) is the charge separation between two valence atoms.

The geopolymer molecular model was constructed by using the Materials Studio 6.0 software package from Accelrys Inc. [27]. The sodium aluminosilicate geopolymer was built based on the work by Sadat et al. [23] in which a Si/Al molar ratio of 2 was used. The cell parameters from the calculation of COMPASS are shown in Table 1. Considering the availability of computational
resource and based on the study of the effect of total atom numbers, the molecular model was constructed by including 5752 atoms in each system. Fig. 1 shows the constructed sodium aluminosilicate geopolymer molecular model. The sodium atoms were then substituted randomly by calcium atoms at 25, 50, 75 and 100%, respectively, in order to study the effect of calcium on the behavior of geopolymer. Fig. 2 shows the models after Na was substituted by Ca at different percentages. Energy minimization was performed on these models to achieve reasonable three-dimensional structure. The MD simulation was performed at 300 K using constant volume (NVT) following the work of Sadat et al. [23]. The resulting geopolymer structure matched the experimental structure from Meral et al. [27]. In order to verify the validity of the geopolymer models and study the change of mechanical properties after Na substitution by Ca, uniaxial compression test was conducted. The periodic boundary condition [28] was applied. The strain rate of the uniaxial compression test was set as 0.002/fs followed by equilibration at constant temperature and volume for 10 ps. The load was applied in the Y direction and the system stress and strain along the Y direction were recorded during the loading.

**Results and discussion**

Fig. 3 shows the uniaxial compressive stress-strain curves from the MD simulations. At all Ca contents, the stress (σ) increases linearly with the strain (ε) at ε = 0 – 0.02. After ε = 0.02, the σ curve starts to yield and σ increases with ε at a slower rate. The failure σ was not predicted from the MD simulation because the COMPASS force field cannot calculate bond break in the cross-linked structure [29], but the results clearly show the increase of modulus and strength of the geopolymer after more Ca is included.

Fig. 4 shows the uniaxial compressive strength of class F fly ash-based geopolymer containing different amount of waste concrete fines (WCF) (which means different Ca contents) from macro-
scale physical experiments [10]. By comparing the MD simulation results and the macro-scale experimental results, it can be clearly seen that the stress values from the MD simulations are much higher than the uniaxial compressive strength (UCS) values from the macro-scale physical experiments. This is due to several reasons [29]. First, the strain rate used in the MD simulations is much higher than that in the macro-scale physical experiments. Second, the structure in the MD simulation is in a periodic boundary condition and can expand infinitely, and the atoms in the MD structure are linked perfectly and the cohesion can be kept. On the contrast, the geopolymer paste specimens in the macro-scale physical experiments contain unreacted source materials and different flaws and voids which can make them significantly weaker than the “pure” geopolymer in the MD simulations.

Fig. 3 clearly shows that the geopolymer gets stronger as more sodium atoms are replaced by calcium atoms. This trend has been proven by many researchers in their macro-scale physical experiments [10,29-31]. Calcium can play three different roles to improve the properties of geopolymer. The first is that calcium cations can keep the charge balance better in the geopolymer system. They are integrated into the geopolymer system through the scheme below [29]:

\[
\begin{align*}
&\equiv Si-O^\cdot Ca^+ + O^- Al + H_2O \rightarrow \equiv Si-O^- Ca^++Al≡ \rightarrow \equiv Si-O^- Al≡ + Ca^{2+} + 2OH^- \\
&\equiv Si-O^- + Ca^{2+} \rightarrow \equiv Si-O^- Ca^+ + H_2O
\end{align*}
\]

The second is the formation of calcium aluminum silicate hydrate (CASH) gel. According to Chindaprasirt et al. [33], the geopolymerization process of a geopolymer system containing calcium can be schematically illustrated by the following reactions:

Reaction (i): Dissolution of SiO₂, Al₂O₃ and calcium sources (CaO and CaSO₄)

\[
SiO_2 + Al_2O_3 + OH^- \rightarrow SiO_2(OH)_2^2- \text{ or } Si(OH)_3^{-1} + Al(OH)_4^- \quad (6)
\]
\[
\text{CaSO}_4, \text{CaO} \xrightarrow{\text{H}_2\text{O}} \text{Ca}^{2+} + \text{SO}_4^{-2} + \text{OH}^- \quad (7)
\]

Reaction (ii): Precipitation reactions

\[
\begin{align*}
\text{Ca}^{2+} + \text{SiO}_2(\text{OH})_{\frac{2}{2}}^- \text{ or } \text{Si}(\text{OH})_{\frac{1}{3}}^- + \text{Al}(\text{OH})_{\frac{4}{4}}^- & \longrightarrow \text{CASH gel} & (8) \\
\text{Na}^+ + \text{SiO}_2(\text{OH})_{\frac{2}{2}}^- \text{ or } \text{Si}(\text{OH})_{\frac{1}{3}}^- + \text{Al}(\text{OH})_{\frac{4}{4}}^- & \longrightarrow \text{NASH gel} & (9)
\end{align*}
\]

Reaction (i) occurs in a high pH environment (pH > 12) and dissolves Si, Al and Ca for geopolymerization and/or hydration. Reaction (ii) is responsible for the strength development [33]. Garcia-Lodeiro et al. [34] investigated that even the environment pH value falls into 9.5 to 12, the NASH gel can fully accept Ca through ion-exchange mechanism to generate (N/C)ASH gel until all Na atoms are replaced by Ca atoms. The calcium exchanging process doesn’t change the NASH gel’s 3D aluminosilicate framework which is different from 2D CASH gel [35]. This type of 3D CASH gel can effectively improve the strength by increasing Si-O-Al bonds in the geopolymer framework [35-37]. The second scheme in reaction (5) is calcium silicate hydrate (CSH) gel. The formation of CSH gel in geopolymer systems have been reported by many researchers [11,39-42], and they have generally arrived at the conclusion that CSH gel also contributes to improving the strength of the geopolymer. However, due to the high alkalinity, the CASH and NASH gel are the principal products of the reaction [10]. It is noted that although the formation of CASH gel is an important factor related to the improvement of geopolymer properties due to the addition of Ca, it is not considered in the current study due to the limitation of the Materials Studio 6.0 software package.

The third is that the unreacted Ca acts as fillers in the geopolymer network and makes the geopolymer denser and thus stronger.
Fig. 3 shows the continuing increase of the geopolymer strength as the calcium content increases; but the macro-scale physical experiments by Ahmari et al. and other researchers [10,37-42] show that the improving effect of calcium only goes to a certain calcium content. For example, in Fig. 4, after the WCF content achieves 50%, continuing increase of the WCF (meaning more calcium) leads to decrease of the strength of the geopolymer paste. According to Ahmari et al. [10], the increased amount of WCF (or calcium) caused formation of Ca(OH)$_2$ and increased the viscosity of the geopolymer paste during the specimen preparation process. In order to acquire the same workability, more water had to be used which caused a direct decrease in strength. In the current research, the MD simulation only considered the geopolymer unhydrated structure, and no water was involved in the construction of the molecular model. As a result, the compressive stress of the geopolymer system simply increases continuously as the calcium content increases. This effect of water will be considered in the next step of research using MD simulations.

**Summary and Conclusions**

This paper presents the preliminary results of MD simulations to study the effect of Ca on the mechanical properties of sodium aluminosilicate geopolymer. Based on the investigation, the following conclusions can be drawn:

1. The MD simulation results show that replacing sodium in the geopolymer system by calcium can effectively improve the strength of the geopolymer product. The general trend is in good agreement with the macro-scale physical experimental results, although the strength value from the MD simulation is significantly higher than that from the macro-scale physical experiments.

2. No water is considered in the current MD study. To fully investigate the effect of Ca on the geopolymerization process, the formation of CASH and CSH gels involving water
needs to be considered. So the next step will be including water in the MD simulations of
geopolymer containing Ca.

Acknowledgements

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Reference


68.


[4] Schneider M, Romer M, Tschudin M, Bolio H. Sustainable cement production present and


5945.


Table 1. The cell parameters for the sodium aluminosilicate system (COMPASS).

<table>
<thead>
<tr>
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Fig. 1. The molecular model of sodium aluminosilicate geopolymer. (blue: Na, pink: Al, red: O, yellow: Si)
Fig. 2. Molecular models of sodium/calcium aluminosilicate geopolymer. (a): after 25% Na substitution; (b) after 50% Na substitution; (c) after 75% Na substitution; and (d) calcium aluminosilicate geopolymer. (blue: Na, green: Ca, pink: Al, red: O, yellow: Si)
Fig. 3. Uniaxial compressive stress-strain curves from MD simulations.
Fig. 4. Uniaxial compressive strength of WCF/FA-based geopolymer paste from physical experiments [10]. SS/N = sodium silicate solution to NaOH solution mass ratio, WCF = aberration for waste concrete fines, and FA = class F fly ash.