THE INFLUENCE OF PHOSPHORUS SLAG ADDITION ON MICROSTRUCTURE AND MECHANICAL PROPERTIES OF METAKAOLIN-BASED GEOPOLYMER PASTES

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In this study, metakaolin plus different weight percent of phosphorus slag (10-100 wt. %) were used in preparation of geopolymer. The compressive strength, phase analysis and microstructure changes were compared with a metakaolin based geopolymer control sample. Results showed that the substitution of slag up to 40 wt. % instead of metakaolin increase the 28 days compressive strength (14.5 %) compared with control sample. This enhancement of strength is related to coexistence of geopolymeric gel and C–S–H gel or C–A–S–H phase by XRD and FTIR study. In slag containing geopolymer samples some microcracks were observed at microstructure that established by volume change during formation of new phase or mismatching of unreacted particle with geopolymeric gel. These microcrack can dominate at high content of slag (above 40 wt. %) substitution and decrease the strength of samples. These results show that it is possible to produce geopolymer cement from waste phosphorus slages.

INTRODUCTION

Geopolymer is inorganic alkali aluminosilicate binder with three dimensional structure formed by mixing alkali silicate solution with aluminosilicate materials. Geopolymer materials have an extensive potential range of applications as a substitute for traditional cements due to their unique properties, such as the ability to withstand elevated temperatures and fire, along with acid and salt resistance, and greatly reduced CO_2 emissions compared to those of Portland cement [1, 2]. The precursors for geopolymers are developed from various sources including the natural source kaolin and industrial wastes or by-products, such as fly ash and ground granulated blast furnace slag (GGBFS) [3]. Geopolymers are generally synthesized by mixing a solid aluminosilicate source, such as fly ash or metakaolin, with a solution containing alkali-metal ions and hydroxide ions. Alkali-metal silicate solutions are often added to promote favorable mechanical properties and control setting times. The basic geopolymer nanostructure is essentially a silica gel network, substituted with tetrahedral Al^{3+}, charge-balanced by alkali-metal cations. The first step in geopolymer formation is the liberation of aluminosilicate species from a solid, typically resulting from alkali-metal hydroxide attack on an aluminosilicate particle [4]. Initially, the surface of the solid particle contacts the activating solution and free SiO_4 and AlO_4 tetrahedral

units formed [5]. With development of reaction of SiO_4 and AlO_4 tetrahedral units are linked and $Na_2O–Al_2O_3–SiO_2–H_2O$ gel grows and finally yields amorphous or semi-amorphous three-dimensional geopolymer binder [6, 7]. Type, particle size and crystallinity of alumino-silicate source, type, concentration and pH of activator and temperature have direct effect on final product. Earlier, most of the research study was focused on geopolymer synthesis from metakaolin, however since last decade much research has been done on fly ash (FA), slags, waste materials and other low cost materials. In summary it can be said that metakaolin is a complete source for production of geopolymers, because it contains a high percentage of silicon and aluminum and has good reactivity and also its control is easy.

In this research, it is trying to proceed making a geopolymeric cement sample (control sample) based on metakaolin with a defined composition and mechanical properties; and finally changes in mechanical and microstructural properties is investigated as a result of metakaolin replacement with waste material (phosphorus slag).

The effect of calcium compounds from different sources such as slag, cement, wollastonite on the meta-kaolin based or fly ash based geopolymer pastes were investigated [8, 9]. The effect of different calcium sources on geopolymerisation is dependent on type of calcium compound such as crystallinity, alkalinity of

activator (pH) and curing temperature. Two main effects on the addition of calcium compounds are reported [8, 9]. One effect is the formation of calcium silicate and/ or aluminate hydrate phases (C–S–H and/ or C–A–S–H) and improvement of geopolymerisation reaction and the other effect is arriving of Ca^{2+} in the geopolymeric binder structure that can acts as a charge-balancing cation or disrupt of three-dimensional aluminosilicate network. In the current study, phosphorus slag containing above amount calcium silicate and some P_2O_5 are added to the metakaolin based geopolymer and investigated mechanical properties and microstructure of resultant geopolymer. The findings of this research would help to reveal the structure of phosphorus slag containing geopolymer and also utilization of this waste material for the beneficial product.

EXPERIMENTAL

Materials

According to previous studies [10] control sample paste (calcined kaolin-based geopolymer) was prepared with calcined kaolin and alkali activator at molar ratio $Na_2O/SiO_2 = 0.6$. Alkali activator consists sodium silicate and sodium hydroxide and metakaolin were obtained from calcination of CC31-kaolin (W.B.B - corporation) at 700°C. The chemical analysis of kaolin and activators are shown in Table 1. The phosphorus slag obtained from an Iranian company that produce P_2O_5 from reaction of calcium phosphate ($Ca_{10}(PO_4)_6F_2$), C and SiO_2. The chemical composition of slag (Table1) shows that calcium silicate base slag contains Al_2O_3 and P_2O_5 components which used for this study. The phosphorus slag was grinded and after passing through sieve (200 mesh) was replaced with different amounts 10 - 100 wt. % instead of metakaolin. Distilled water was used throughout this study.

Specimens preparation

For preparation of the specimens, molar ratio $Na_2O/Al_2O_3 = 0.8$ and mass ratio W/C = 0.53 for all specimens were used. The activating alkali solution was prepared by dissolving NaOH pellets in distilled water and mixing with sodium silicate solution and was then stored for one day prior to use to allow equilibration. Metakaolin (MK)

and phosphorus slag (PS) powders with nine different ratios between MK and PS was added into the above pre-mix alkaline solution and further mixed for 5 minutes. The MK / (MK + PS) mass ratios being 0; 0.1; 0.2; 0.4; 0.5; 0.6; 0.8; 0.9 and 1. These particular ratios were chosen so as to provide for equal moles of water present in the structures of all the matrices synthesized. After mixing, the geopolymeric pastes were poured into cubic steel mold (50 mm each side) which were then vibrated for 2 min. In order to prevent the evaporation of mixing water and the carbonation of the surface, the specimens were covered by plastic film during the setting and hardening process. After hardening at room temperature for 24 h the specimens were removed from molds. The de-molded specimens cured at room temperature in normal atmosphere condition for 7, 14, 21 and 28 days. At least 3 specimens were made for each formula. Then compressive strength testing is performed and average value is served as the ultimate compressive strength.

The fragments of the selected formula were collected after compressive tests for microstructure analysis. Some of them were used to conduct SEM-EDX analysis and the others are further finely crushed for XRD and FTIR analysis.

Nomenclature and sample composition

Samples were classified by the source of solid aluminosilicate, type of material replaced, percent of the replacement (%) and curing time. Samples were named using the following nomenclature:

aM - Xb

where *a* indicates the curing time, *M* indicates source of solid aluminosilicate (*M* = Metakaolin), *X* indicates the type of material replaced (*S* = Slag) and *b* indicates the percent of the replacement.

METHOD OF ANALYSIS

FTIR analysis

Fourier transform infrared spectroscopy (FTIR) is performed on a SHIMADZU-FTS 8400 FTIR using KBr pellet techniques. The resolution and number of scans used in FTIR collection were 2.0 cm^{-1} and 16, respectively.

Table 1. Chemical composition of the starting materials used.

Material	P_2O_5	Al_2O_3	SiO_2	K_2O	Na_2O	Fe_2O_3	TiO_2	CaO	MgO	L.O.I
Kaolin	--	31.1	54.25	0.9	--	0.91	0.59	0.20	0.48	11.51
Na_2SiO_3 (aq)	--	--	25.5	--	13.1	--	--	--	--	61.4
NaOH (10 M) (aq)	--	--	--	--	23.74	--	--	--	--	76.2
phosphorus slag	1.79	6.97	37.92	0.68	0.38	0.62	--	46.45	1.2	2.46

XRD analysis

X-ray powder diffraction is recorded on a Philips PW1800 spectrometer with the following testing parameters: 40 kV, 30 mA, Cu (Kα) Radiation. The XRD patterns obtained by a scanning rate of 1° per min from 2θ = 5° to 60° and steps of 2θ = 0.04°.

SEM analysis

VEGA\\TESCAN SEM is used to characterize the microstructure and chemical compositions of the fully reacted geopolymeric specimens. The following test parameters are employed in this study: accelerating voltage of 15 keV, pressure and relative humidity in sample chamber of 4.2 Torr and R.H. 80 % respectively.

RESULTS AND DISCUSSION

Compressive Strength

Figure 1 shows compressive strength geopolymeric samples replaced with slag, preposition to percentage substitution at different curing times. Overall according to strength results we can say:

Replacing of the phosphorus slag instead of metakaolin to 80 wt. % will be reduced compressive strength toward the control sample in curing time of 7 days.

Replacing of the slag instead of metakaolin (10 - 100 wt. %) will be led to increasing of compressive strength of the geopolymeric samples toward the control sample in curing times of 14 and 21 days.

In curing length 28 days with replacing of slag instead metakaolin to 40 wt. % led to increasing of compressive strength, however, the addition of slag was destructive if it was added in a significant amount (40 - 90 wt. % of total mass).

Previous studies have shown that the addition of limited amount calcium has generally positive effect on the mechanical properties of the geopolymeric binder, but the exact role of calcium during the geopolymerisation process remains unclear [11-13]. Phase

separation between alkali-aluminosilicate (i.e. geopolymer) and partially Al-substituted calcium silicate hydrate (C–A–S–H) gels has been observed in a number of Ca-containing geopolymer systems [13, 14]. It has also been suggested, but never definitively proven, that Ca^{2+} is capable of acting as a charge-balancing cation within the geopolymeric binder structure [14].

For statement of decreasing compressive strength of slag substituted geopolymer pastes in 7 days curing time in comparison with control sample must be said that dissolution of silicon and aluminium from the aluminosilicate source (metakaolin in this case) governs the initial stage of geopolymerisation. The formation of a geopolymeric gel depends on the availability of dissociated silicate and aluminate monomers in the alkaline medium, which is further dependent on the extent of dissolution of these two species from the original aluminosilicate source. In the presence of soluble calcium species, the dominant reactions dependent on pH, SiO_2/Al_2O_3 ratio and amount of calcium may become more complex. Under these circumstances calcium could precipitate as $Ca(OH)_2$, C–S–H and C–A–S–H, lowering the alkalinity of the medium and decreasing driving force for dissolution of silicon and aluminum that hindering the formation of the geopolymeric gel and cause strength development to delay [13, 14]. It seems that at 7 days curing, the precipitation of C–S–H, C–A–S–H and low amount formation of geopolymer gel led to decreasing of compressive strength slag containing geopolymer pastes toward the control sample.

Increasing of compressive strength of the geopolymeric samples in curing times of 14, 21 and 28 days could be due to development of geopolymer network gel after precipitation of initial calcium containing gels. With decreasing significant levels of dissolved calcium, silicate and aluminate monomers will react together to form a geopolymer in an alkaline environment. So we can say that increasing of compressive strength in geopolymeric samples substituted with slag, are because coexistence of geopolymeric alkali aluminosilicate gel and C–S–H or C–A-S–H gels. As noted previously, strength of samples at curing time of 28 days is reduced over replacement 40 % slag instead of metakaolin. The reason for this behavior seems to be clarified by examining microstructure of these samples.

Infrared spectroscopy characterization

Figure 2 shows FTIR spectra of the slag, control sample (28M) and geopolymeric samples replaced with 40, 50, 100 wt. % of phosphorus slag after 28 days curing. The geopolymer cement samples contain geopolymer gel with empirical formula similar to $Na_n\{-(SiO_2)_z-AlO_2-\}_n.wH_2O$ and unreacted metakaolin and/or phosphors slag particle. The slag spectrum contains wide bands at 518, 707, 1008, 1429 and 3442 cm⁻¹. In slag spectrum signal at about 1008 cm⁻¹
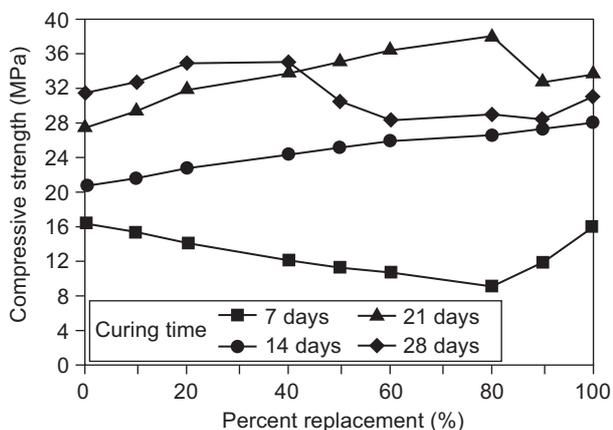

Figure 1. Compressive strength versus wt. % added slag.

correspond to the asymmetric stretching vibration Si–O–Si or Si–O–Al bond, but this signal appear at 1020 cm^{-1} in control sample (28M). The peak shift of slag containing geopolymer cement samples in comparison with control sample to lower wavenumber (1012, 1008 and 995 cm^{-1} versus 1020 cm^{-1}) and decreasing of its intensity related to formation of new geopolymeric product. This shift to lower wave number indicates that high level substitution of Al instead of Si in tetrahedral. Decreasing of peak intensity indicates formation of less content of geopolymeric gel, that otherwise will form hydrated calcium silicate products such as C–S–H or C–A–S–H gels. As described presence of calcium in composition and precipitation of calcium containing gels lowering the alkalinity of the medium and thus the driving force for dissolution of silicon and aluminium that in turn decreased the geopolymeric gel [15, 16]. The broad bands in the region of 1650 - 3480 cm^{-1} are characterized by the spectrum stretching and deformation vibrations of O–H and H–O–H groups from the weakly bound water molecules. Intensity of these peaks decreased with substitution of slag instead metakaolin. The peaks seen in all geopolymer samples at around 1470 cm^{-1} have been attributed to stretching vibration of C–O which is due to efflorescent of geopolymers. Also it can be seen that intensity of peak decreased with replacing of the slag, which attributed to reduction of free alkali in samples [16].
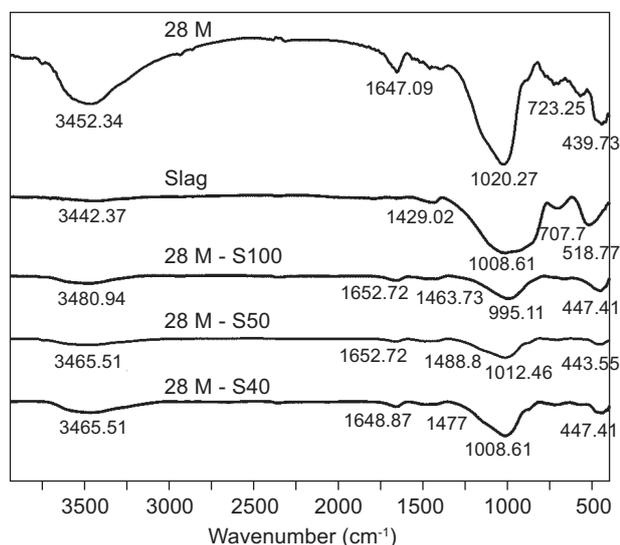
samples have not have a clear peak and is called X-ray amorphous. The peaks in the control sample spectrum are also related to metakaolin impurities (quartz, muscovite and halloysite). The similar large diffused halo peaks at about 2θ = 20 – 40° in diffraction pattern of the control sample and other samples replaced with slag, indicate that amorphous product (geopolymer) have formed. Peaks in the diffraction pattern of samples 28M-S40 and 28M-S50 (2Θ = 9.1, 12.7 and 25.3) are shown with dashed circle, indicating the formation of hydrated calcium aluminosilicate (C–A–S–H) phase which some researcher reported its formation earlier [17, 18]. These peaks are not present in pattern of the control sample. Those peaks disappear with full replacing slag (100 wt. %) instead of metakaolin which the reason is unknown.
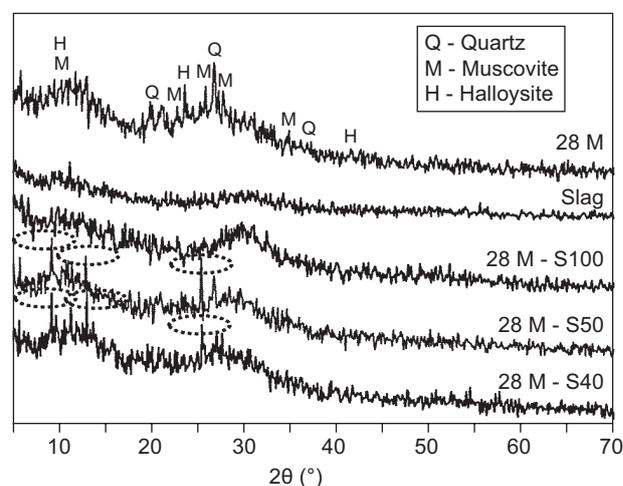

Figure 3. XRD diffraction patterns of the slag, control sample and sample replaced with different percentages of slag.

SEM analysis

SEM image and EDX analysis of geopolymer sample 28M-S40 is presented in Figure 4. As seen in the figure this sample is composed of two phases. SEM-EDX analysis shows that phase (1) shown in figure is geopolymeric matrix with a small percentage of calcium, and phase (2) also is related to the hydrated calcium aluminosilicate phase or unreacted slag. This analysis also shows that calculated Si/Al and Na/Al ratio toward predicted ratios for composition (phase 1) is less and more respectively. The existence of little amount of calcium in geopolymeric matrix is probably an indication of lack of Na$^+$ ions in charge-balancing of network and minor diffusion of calcium to the inside of geopolymeric matrix. It can also be observed in Figure 4 that some cracking has occurred in the sample. This is not believed to be due to sample preparation for SEM, but rather due to volume changes that would occur when forming an amorphous to semi-crystalline CSH gel within a partially hardened geopolymer gel.

Figure 2. FTIR spectra of the slag, control sample and sample replaced with different percent of slag.

X-Ray Diffraction Characterization

XRD diffraction patterns of the slag, control sample (28M) and samples replaced with different percentages of slag (40, 50 and 100 %) are shown in Figure 3. As can be seen the slag and slag containing geopolymer

It is suggested that high amount of calcium dissociated from the surface of phosphorus slag particles will precipitate from the alkaline medium as $Ca(OH)_2$ or C-S-H and C-A-S-H gels and rare amount of calcium arrive to geopolymer gel structure, which may explain why traces of calcium could be detected in the rich aluminosilicate phase. However, it is still unclear how the calcium is structurally bound within the aluminosilicate phase.

It seems coexistence of geopolymeric and hydrated phase should be made increasing of final strength, but on the other hand presence of cracks will be disrupted development of compressive strength. Consequently the amount of crack in geopolymeric matrix increased with increasing slag replacement instead of metakaolin and more formation of secondary hydrated phases that cause the strength reduces further.

CONCLUSION

In this study, the effect of substitution of phosphorus slag on the mechanical and microstructure changes in metakaolin based geopolymers was investigated. This slag has amorphous structure and contains CaO = 46 wt. % and SiO_2 = 38 wt. %. Results show that the substitution of slag up to 40 wt. % instead of metakaolin is possible, and an enhancement in 28 days compressive strength (14.5 %) compare to control sample. The obtained results were explained on the basis of XRD analysis, FTIR spectra change and microstructure development. The X-ray patterns show the presence of calcium aluminosilicate hydrated (C-A-S-H) for samples which contain slag in addition of geopolymeric gel phase. Coexistence of both geopolymeric gel and C-A-S-H gel give rise to the enhancement of mechanical strength. The microstructure changes on the molecular level by FTIR spectroscopy were shown that new gel structure in comparison with control sample were developed on the slag containing samples. SEM microscopic images also confirm the X-ray pattern results and show presence of hydrated phase and unreacted particles, alongside geopolymeric phase. There have been micro crack in microscopic images from samples that contain slag which cause a decrease in mentioned samples' strength.

Figure 4. SEM image and EDXA of geopolymer sample of 28M-S40.

REFERENCES

1. Fareed Ahmad M., Fadhil Nuruddin M., Shafigh N.: World Academi of Science, Engineering and Technology *50*, 8 (2011).
2. Duxson P., Ferna´ndez-Jime´nez A., Provis J. L., Lukey G. C., Palomo A., Van Deventer J. S. J.: J. Mater. Sci. *42*, 2917 (2007).
3. Fernandez-Jimenez A., Palomo A.: Cem. Concr. Res. *35*, 1984 (2005)
4. Lee W. K. W., Van Deventer J. S. J.: Colloids Surf. *211*, 49 (2002)
5. Yunsheng, Z., Wei, S., Zongjin, L., Ceramics-Silikaty *53*, 88 (2009).
6. Rovnanik P.: Construction and Building Materials *24*, 1176 (2010).
7. Najafikani E., Allahverdi A., Ceramics-Silikaty *53*, 195 (2009).
8. Yip C.K., Lukey G.C., Provis J.L., Van Deventer J.S.J.: Cement and Concrete Research *38*, 554 (2008).
9. Temuujin J., Riessen A. Van., Williams R.: Journal of hazardous materials *167*, 82 (2009).
10. Soleimani M., Naghizadeh R., Mirhabibi A.R. in: 8th Iranian Ceramic Congress, IUST University, Tehran, 2011.
11. Granizo M.L., Alonso S., Blanco-Varela M.T., Palomo A.: J. Am. Ceram. Soc. *85*, 225 (2002).
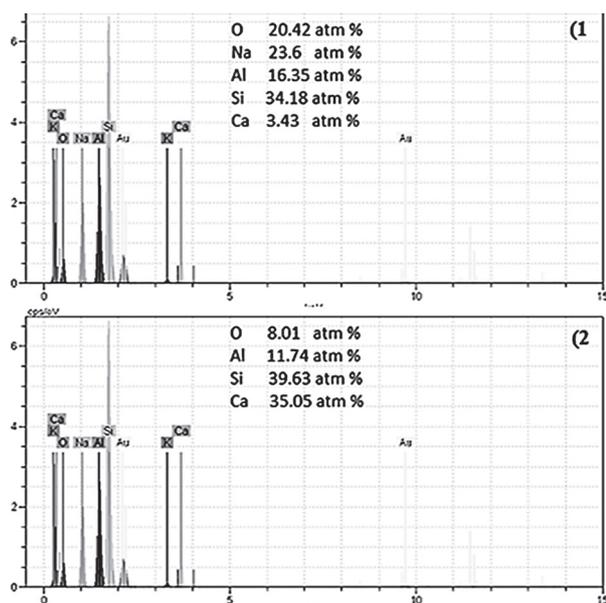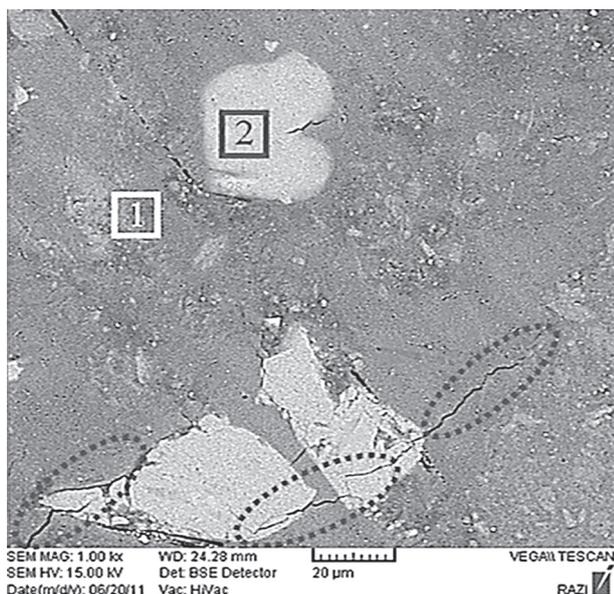
12. Yip C.K., Van Deventer J.S.J.: J. Mater. Sci. *38*, 3851 (2003).
13. Yip C.K., Lukey G.C., Van Deventer J.S.J.: Cem. Concr. Res. *35*, 1688 (2005).
14. Manzano H., González-Teresa R., Dolado J.S., Ayuela A.: Materials of Construction *299*, 7 (2010).
15. Palomo A., Fernandez-Jimenez A., Kovalchuk G., Ordonez L.M., Naranjo M.C.: Journal of Materials Science *42*, 2958 (2007).
16. Komnitsas K., Zaharaki D.: Minerals Engineering *20*, 1261 (2007).
17. Macphee D., Garcia-Lodeiro I.: 2nd International Slag Valorisation Symposium, Leuven 2011.
18. Tailby J., MacKenzie K. J. D.: Cement and Concrete Research *40*, 787 (2010).

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