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Title: Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure

Article Type: Research Paper

Keywords: metakaolin; rice husk ash; geopolymer; sodium hydroxide; tensile strength; microstructure.

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Abstract: High cost, less workability and drying shrinkage have been raised among factors affecting the promotion of metakaolin (MK) geopolymers. The objective of the present work is to study the performance of fresh and hardened metakaolin geopolymer pastes in which metakaolin is partially replaced by 12.5 to 50 % Rice Husk Ash (RHA) in the solid mixes in the presence of 10 M sodium hydroxide solution at ambient conditions of 20 ± 3 °C and 70 ± 5 % relative humidity with liquid/solid ratio of 0.95. Chemical analysis and specific gravity test were done on raw materials and then consistency and setting time tests were done on fresh geopolymer pastes. Hardened products at 7 and 28 days of curing underwent tensile strength measurements according to ASTM C 307-03 (2012). Samples at 28 days of curing also underwent SEM/EDX and thermogravimetric analyses. Replacement of MK with up to 25 % RHA showed various advantages compared to the mixture of MK with no RHA as replacement. The workability of fresh pastes improved as suggested by decrease in consistency of MK-RHA blends at fixed liquid/solid ratio. For hardened pastes, the SEM/EDX analyses suggested that the presence of RHA affected Si/Al ratios of geopolymers, with consequences on their polycondensation reactions gels. Beneficial effects were evidenced by the improvements in tensile strength. Enhancement of tensile strength resulted from the densification of the matrix and the reduction of the negative effect of drying shrinkage and associated micro-cracks.

To the Editor in Chief of **Construction and Building Materials** journal

Subject: Publication of our revised article CONBUILDMAT –D-17-06603

We hereby apply for the publication of our research paper entitled “**Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure**

” in your journal.

The article is an original research contribution on blended metakaolin with rice husk ash for the production of geopolymers with sodium hydroxide at ambient temperature. Chemical characteristics of raw materials were determined. Consistency and setting time of fresh pastes were evaluated. Tensile strength, microstructure and thermogravimetric characteristics of hardened products were determined at 7 or 28 days of curing. Discussion of results showed that up to 25 % blends of rice husk ash in metakaolin can contribute to increase tensile strength of mixtures , to improve its workability and to reduce negative effect of drying shrinkage.

The results can contribute to improve the promotion of sodium silicate free metakaolin geopolymers.

While waiting the publication, accept our best regards.

Yaoundé, 19/04/2018

For the authors

NDIGUI BILLONG (Ph.D) (corresponding author)

Senior Researcher. The Local Materials Promotion Authority (MIPROMALO), P.O.

Box: 2396 Yaoundé, Cameroon.

To the Editor in Chief of Construction and Building Materials journal

Subject: attestation of no conflict of interest about article CONBUILDMAT –D-17-06603

We hereby attest that there is no conflict of interest about our submission entitled
“**Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure**” in your journal.

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Table 1: Major oxides of MK and RHA (wt %)

Oxides	MK	RHA
SiO ₂	58.50	93.20
Al ₂ O ₃	36.80	0.58
Fe ₂ O ₃	0.61	0.20
CaO	0.71	0.56
MgO	0.11	0.30
Na ₂ O	0.31	0.08
K ₂ O	2.00	3.04
L.O.I.	0.11	1.20
Total	99.15	99.16

Table 2. Dosage of constituents in 500 g of solid mix (MK and RHA).

Samples	MK		RHA	
	(g)	(%)	(g)	(%)
G0	500.0	100.0	0.0	0.0
G12.5	437.5	87.5	62.5	12.5
G25	375.0	75.0	125.0	25.0
G50	250.0	50.0	250.0	50.0

Table 3. Effect of RHA on consistencies the paste after 5 minutes of mixing.

Samples	Penetration (cm)
G0	20
G12.5	40
G25	40
G50	40

Table 4. Atomic composition of samples spots by EDX

Element	Composition of spots of samples (atomic %)			
	G0	G12.5	G25	G50
O	62.05	59.23	60.18	59.41
Na	9.58	13.70	13.34	11.66
Mg	/	/	/	0.15
Al	12.55	10.09	9.60	6.87
Si	14.81	14.64	15.64	20.18
P	0.47	1.29	0.12	0.19
S	/	/	/	0.08
Cl	/	0.09	/	/
K	0.53	0.72	0.78	0.82
Ca	/	0.24	0.34	0.65
Totals	99.99	100	100	100.01
Si/Al	1.18	1.45	1.62	2.94

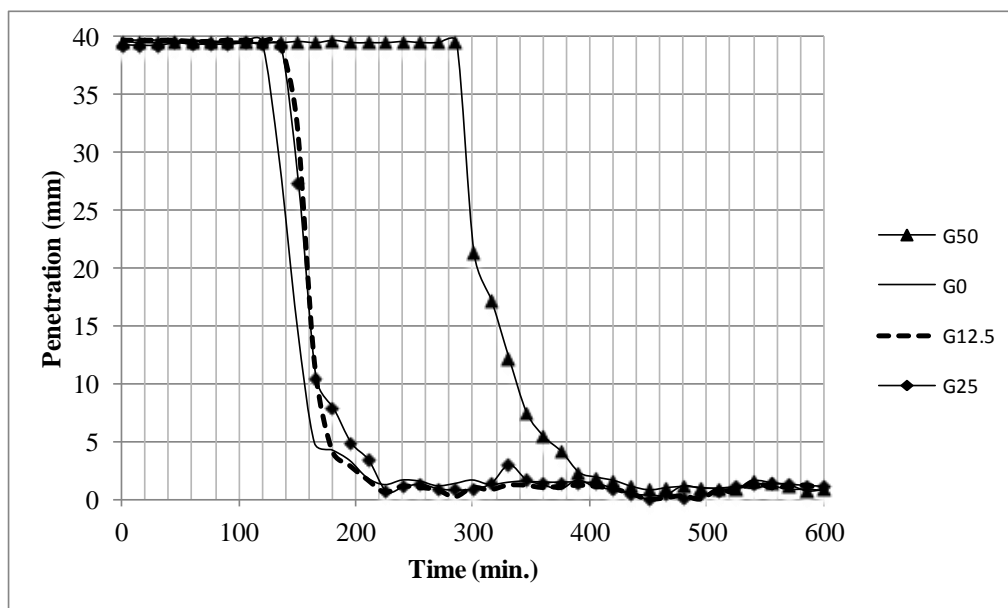


Fig. 1. Effect of RHA on setting of mixes

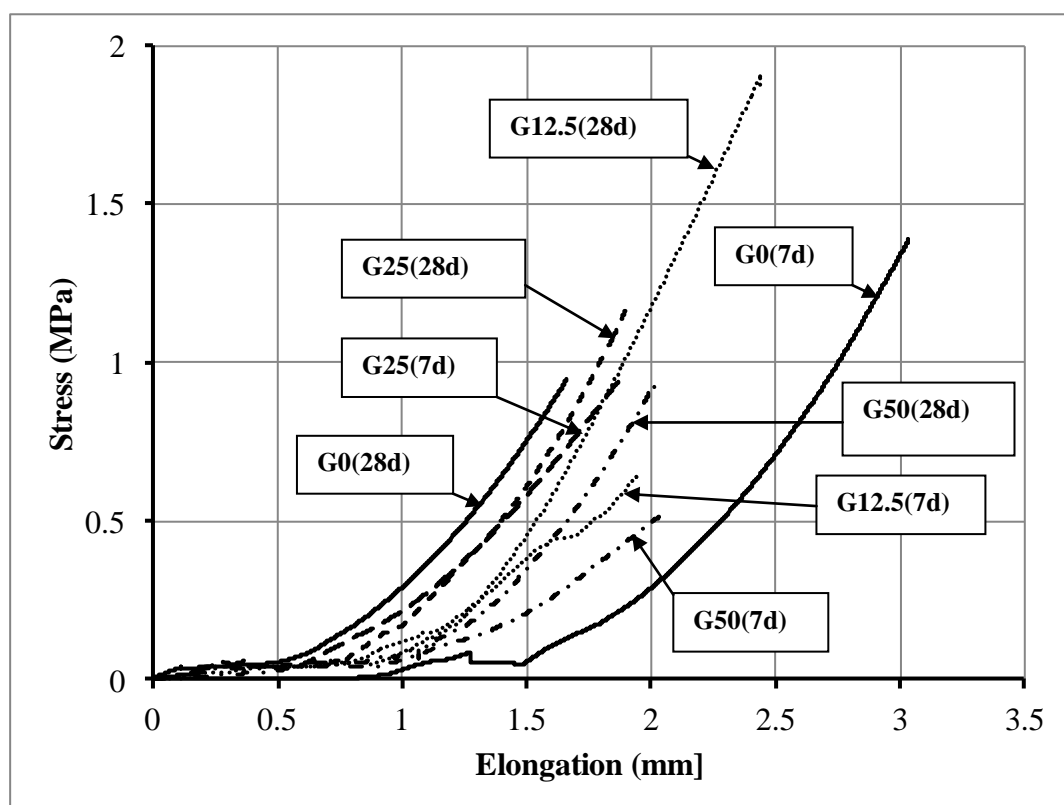


Fig. 2. Stress-elongation curves of hardened geopolymer pastes at 7 and 28 days (d)

Figure

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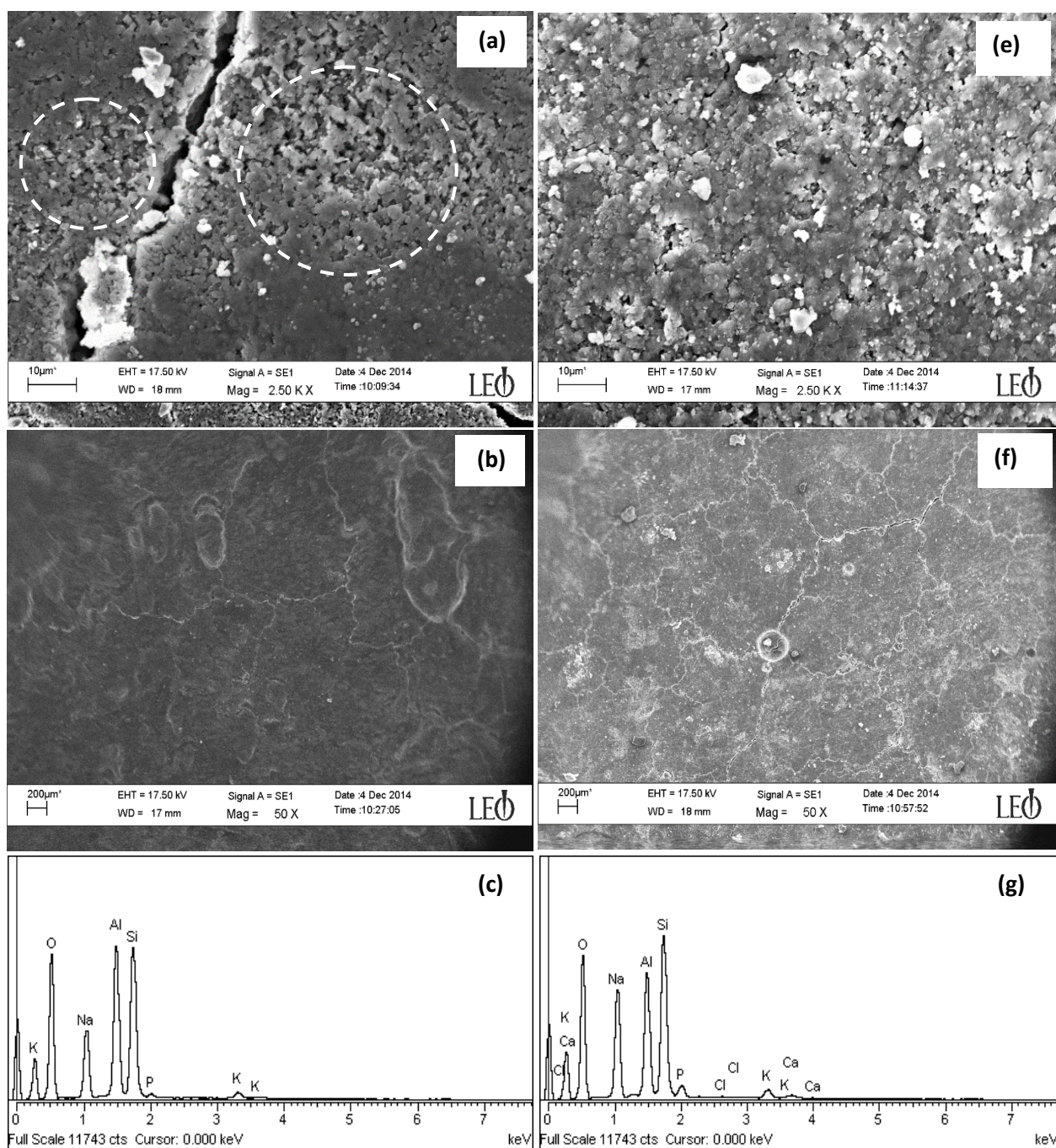


Fig. 3. Microstructure of geopolymer with 0% RHA (left) and 12.5 % RHA (right): high (a,e) and low (b, f) magnifications; (c, g): EDX spectrographs.

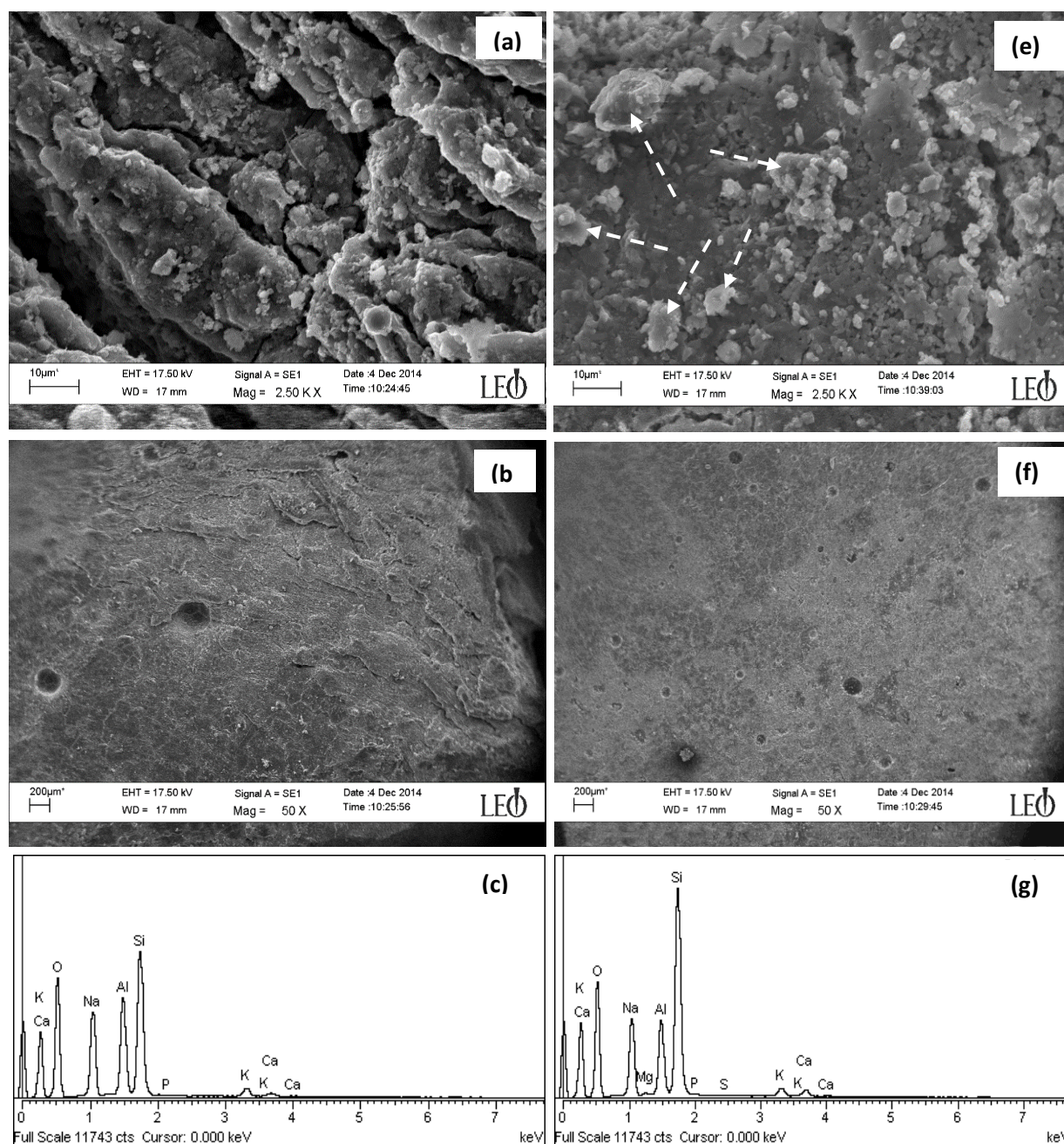


Fig. 4. Microstructure of geopolymer with 25 % RHA (left) and 50 % RHA (right): high (a,e) and low (b, f) magnifications; (c, g): EDX spectrographs.

Figure

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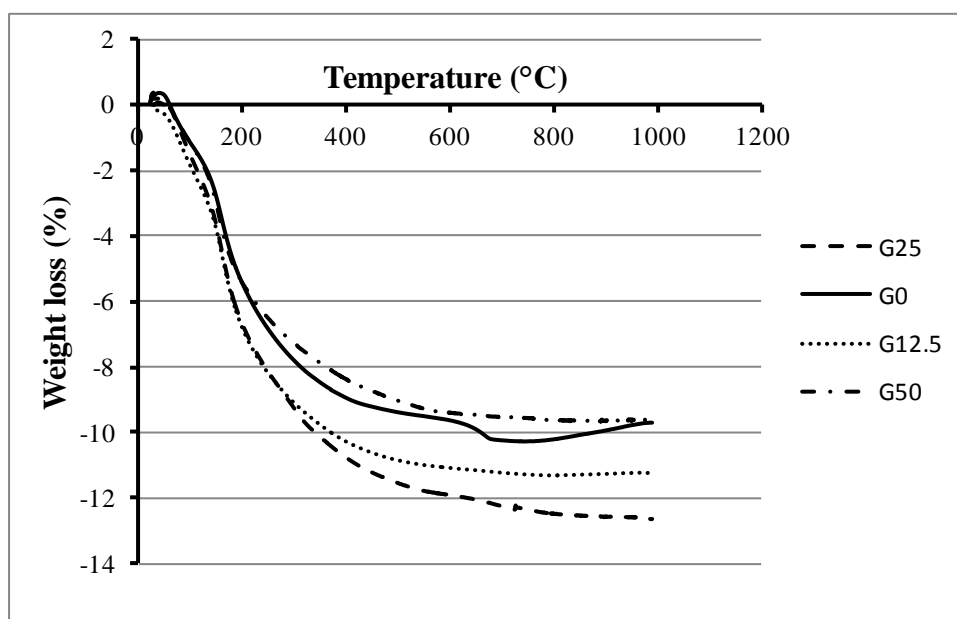


Fig. 5. TG thermograms of hardened geopolymers at 28 days of curing.

To the Editor in Chief of Construction and Building Materials journal

Subject: Revision note of our article Ref. N° CONBUILDMAT-D-17-06603

We hereby submit the revised version of our research paper entitled “Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure” taking in consideration remarks of reviewers in which we almost completely agreed.

1) From comments of reviewer 1: The manuscript have checked again and language errors have been corrected;

2) From comments of reviewer 2:

-The word “geopolymer paste” has been used, instead of “geopolymer” only;

-The title of Standard ASTM C 307-03 has been mentioned and potential applications (non-structural uses, repairs, fillings, surfacings, grout works) of the geopolymer elaborated have been mentioned at the introduction.

3) From comments of reviewer 3:

- References for XRD information of the raw materials have been indicated and their specific gravity data have been provided;

- The molarity (10M) used in the study was on the basis of previous works that was referenced. High pH is required to promote dissolution and hydrolysis of the aluminosilicate and to initiate geopolymerization;

- The description of testing method for setting test have been shortened;

- More discussions have been provided on setting test results with more explanations why up to 25%RHA is not consistent as other RHA contents;

- More articles (03 more) have been cited and more discussions have been provided about the result of tensile strength. The misunderstanding about “Geopolymerization

yielding strong or weak bonds in the production process” have written in a more understandable way;

- Figure 1 have been delated;
- Figures 3 and 4 have been combined and a better legend have been provided to show the effect of RHA;
- For clarity reason, we didn't succeed to combine 04 figures having 12 sub figures (Fig. 5 to 8) but we transformed them to 02 figures instead of 04. Figure 5 and 6 were combined and Figure 7 and 8 were combined. It gives more view on the effect of RHA on microstructure;
- The dilute effect of RHA has been considered on the conclusion

From comments of reviewer 4:

- The introduction has been revised to avoid misunderstanding about the reduction of sodium silicate;
- For homogeneity, we harmonized the use G0, G12.5, G25 and G50 as codes of our sample in the text, figures and tables;
- Globular grains of polysialates have been indicated in the micrograph
- Unreacted species have also been pointed in the micrograph.

While waiting the publication, accept our best regards.

Yaoundé, 19/04/2018

For the authors

NDIGUI BILLONG (Ph.D) (corresponding author);

Senior Researcher;

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Highlights

- Up to 25 % RHA can be used as blends in sodium silicate free metakaolin geopolymer;
- RHA has a dilute effect on pastes which improved the workability of the paste;
- RHA acted as setting retarder with effect not significant at up to 25 % RHA;
- RHA reduced brittleness and eliminated long term reduction in strength of samples;
- RHA reduced voids and densified the matrix of hardened geopolymer pastes.

Performance of sodium silicate free geopolymers from metakaolin (MK) and Rice Husk Ash (RHA): Effect on tensile strength and microstructure

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Abstract

High cost, less workability and drying shrinkage have been raised among factors affecting the promotion of metakaolin (MK) geopolymers. The objective of the present work is to study the performance of fresh and hardened metakaolin geopolymer pastes in which metakaolin is partially replaced by 12.5 to 50 % Rice Husk Ash (RHA) in the solid mixes in the presence of 10 M sodium hydroxide solution at ambient conditions of 20 ± 3 °C and 70 ± 5 % relative humidity with liquid/solid ratio of 0.95. Chemical analysis and specific gravity test were done on raw materials and then consistency and setting time tests were done on fresh geopolymer pastes. Hardened products at 7 and 28 days of curing underwent tensile strength measurements according to ASTM C 307-03 (2012). Samples at 28 days of curing also underwent SEM/EDX and thermogravimetric analyses. Replacement of MK with up to 25 % RHA showed various advantages compared to the mixture of MK with no RHA as replacement. The workability of fresh pastes improved as suggested by decrease in consistency of MK-RHA blends at fixed liquid/solid ratio. For hardened pastes, the SEM/EDX analyses suggested that the presence of RHA affected Si/Al ratios of geopolymers, with consequences on their polycondensation reactions gels. Beneficial effects

were evidenced by the improvements in tensile strength. Enhancement of tensile strength resulted from the densification of the matrix and the reduction of the negative effect of drying shrinkage and associated micro-cracks.

Key words: Metakaolin; Rice husk Ash; Geopolymers; Sodium hydroxide; Tensile strength; Microstructure.

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Introduction

The search for alternative binders to mitigate the high demand of energy and greenhouse gas emissions faced by the Portland cement industry is of great concern [1]. Geopolymers can be a promising alternative binder. They are materials originated by inorganic poly-condensation so called “geo-polymerization” and can gain reasonable strength in a short time under adequate curing at temperatures between 20 and 400 °C [2, 3]. Unlike ordinary Portland or pozzolanic cements, geopolymers do not need calcium silicate hydrates for strength gain but utilize the polymerization of silica and alumina precursor (e.g from metakaolin, fly ash, slag) and a solution of alkali-salts, generally consisting of a mix of sodium hydroxide and sodium silicate or potassium hydroxide and potassium silicate to attain structural strength [4 – 6]. The result is a mixture of gels and crystalline compounds that eventually harden into new strong compounds. Alkali activation of aluminosilicates materials that leads to geopolymers represents a complex process that is not yet fully described [7, 8]. In that reaction, the strong alkaline solution breaks the Si-O-Si bonds of the aluminosilicate and new phases are formed by the penetration of Al atoms into the original Si-O-Si structure.

These phases are mostly aluminosilicates gels or zeolite precursors. Their composition can be characterized by the formula $M_n[-(\text{Si-O})_z\text{-Al-O}]_n \cdot w\text{H}_2\text{O}$, where M can be K, Na or Ca atom, n the degree of polycondensation, z is 1, 2 or 3 and w the binding water amount. In diluted suspensions ($w > 1$), mostly crystalline zeolite type products like analcime and hydro-sodalite are formed. For higher concentration of the solid phase in the suspension ($w < 1$), amorphous products as poly-sialates depending on the Si/Al ratio are predominant. The network is formed by SiO_4^- and AlO_4^- tetrahedrons linked by oxygen bridges. Chains or rings united by Si-O-Al bridges are then formed. The negative charge of Al atom that is present in the coordination 4 is compensated by positive Na^+ , K^+ or Ca^{2+} ions. Based on their monomeric units, three different inorganic polymers can be distinguished: poly-sialate (PS) (-Si-O-Al-O-) with Si/Al = 1; poly-sialatesiloxo (PSS) (-Si-O-Al-O-Si-O-) with Si/Al = 2 and polysialatedisiloxo (PSDS) (-Si-O-Al-O-Si-O-Si-O-) with Si/Al = 3.

Metakaolin is the product of calcination of kaolinite rich clay at (600 - 850 °C) [11] depending on the purity and the crystallinity of the initial clay. The geopolymers with metakaolin as aluminosilicate have shown promising results in previous works [12-14] but they have not been considered as serious alternative binders to Portland cement. High cost due to the fact that metakaolin is not a by-product, less workability and brittleness due to high water demand, drying shrinkage and cracking were pointed as problems affecting the promotion of metakaolin geopolymers [13, 15]. To propose new methods of elaborating geopolymers, Kusbiantoro et al. [16] studied compressive strength of microwave incinerated rice husk ash and fly ash geopolymer. He et al. [17] characterized red mud/rice husk ash base geopolymers. In both studies sodium silicate was used with sodium hydroxide as alkaline solution. But, developments in the fabrication of pure silica from RHA have shown that sodium silicate can be obtained in the process [18-22]. RHA has also shown in previous research, promising application as Supplementary Cementing Material (SCM) in concrete or

as pozzolanic materials with hydrated lime due to its high reactivity [23 - 25]. Bouzon et al. [26] observed similarity in strength when they used a suspension of RHA/NaOH boiled in a reflux system in replacement of commercial water glass or sodium silicate for fluid catalytic cracking (FCC) geopolymer design. Tchakouté et al. [27] and Kamseu et al. [28] recently used RHA in the production of geopolymers with metakaolin but they focused on the synthesis of sodium silicate using RHA. Less attention was given on partial replacement of metakaolin by RHA before the reaction of the obtained solid mix with sodium hydroxide solution.

The objective in the present work is to study the performance of metakaolin geopolymer pastes in which metakaolin is partially replaced by 12.5 to 50 % RHA in solid mixes, in the presence of 10 M sodium hydroxide solution as alkaline solution at ambient temperature. It was hypothesized that the amorphous silica from RHA will in situ react with sodium hydroxide to form higher Si/Al ratio silicate gel which will contribute to the polycondensation reaction to improve the performance of the resulted geopolymer. The chemical composition and the specific gravity of raw materials were determined. The consistency and setting time of fresh geopolymer pastes were tested. Hardened products underwent tensile strength test on the basis of the standard test method for tensile strength of chemical resistant mortars, grouts and monolithic surfacings, ASTM C 307-03 (2012) [29] for potential use of the paste for non-structural applications, repairs and grout works (filling and sealing) in construction. Scanning Electron Microscopy coupled with Energy Dispersive Spectrometry (SEM /EDX) and thermo-gravimetric (TG) analyses were also applied on hardened pastes samples.

2. Materials and experimental procedure

2.1. Characteristics of materials used in study

An industrial MK (Metastar 501,) from highly refined kaolin, by Imerys, United Kingdom and Rice Husk Ash (RHA) obtained by firing rice husk from a paddy rice mill in Bamenda (North-West Region of Cameroon) at 700 °C for 2 hours were the raw materials used. X-Ray Diffractometry (XRD) of a sample of MK and RHA were previously performed. Kuenzel et al. [30] found that MK was consisted of 96.2 % of amorphous phase and 3.6 % insoluble residue as quartz and kaolinite then Beleuk et al. [31] indicated that RHA was in amorphous nature with minor quartz impurities. Thermal activation of the raw materials transformed them to an amorphous and reactive state. The specific gravity of MK and RHA powders obtained by the pycnometer with helium gave respectively 2.5 and 2.2 g/cm³. The chemical composition of raw materials was determined by XRF method, using a Bruker S4 Pioneer wave lengths dispersive (WD-XRF) spectrometer. Results presented in Table 1 showed that MK mainly consisted of SiO₂ and Al₂O₃ whereas RHA has mainly SiO₂.

The alkaline solution was a 10 M sodium hydroxide (NaOH) solution obtained by dissolving laboratory grade pellets of NaOH (from Fisher Scientific UK, purity 97 %) in de-ionized water. The concentration of NaOH was chosen on the basis of previous optimization works [32]. The solution was prepared 24 hours before its use and kept in a container with a lid.

2.2. Preparation of geopolymer mixtures and characterization

MK and RHA were mixed in various proportions (Table 2) and ball milled together for one hour. Samples of each powder were collected, mixed with NaOH solution at a liquid/solid ratio of 0.95 and then stirred until a homogeneous paste was obtained. The liquid/solid ratio used was on the basis of previous works [33 - 35] that showed that the optimal liquid/solid ratio for optimal mechanical performance of MK geopolymers is almost 1. The chosen liquid/solid ratio permitted to obtain acceptable initial workability on the reference sample having 100 % MK and 0% RHA.

2.3. Characterization of fresh and hardened geopolymers

The consistency of geopolymer pastes was tested using a manual Vicat apparatus equipped with the consistency plug. The more the penetration of the plug is, the less is the consistency. The initial and final setting time test of pastes was carried out with an automatic penetrometer (Vicatron) equipped with a penetration needle, in accordance with EN 196-2005 standard. Parts of the fresh geopolymers paste were placed in briquette gang molds on the basis of ASTM C 307-03 (2012) standard, vibrated for 2 minutes and removed from those molds after 24 hours in ambient temperature of 20 ± 3 °C and 70 ± 5 % humidity. After 7 and 28 days of curing, the briquettes were tested for tensile strength at a testing rate of 1 mm/minute, using a Hounsfield H10 KM equipment. The stresses of samples (in MPa) were recorded as a function of their elongations (in mm). The stress-elongation curves of samples having the highest maximum stress were compared. Thereafter, microstructure and thermogravimetric analyses of hardened samples were respectively examined using a Carl Zeiss SMT 1430 Scanning Electron Microscope (SEM) fitted with Solid state Backscattered Detector (SBD), also equipped with INCA-SUITE version 4.01 of Oxford instrument linked with an Energy Dispersive X-ray (EDX) and then a TA Instrument Hi-Res TGA 2950 thermogravimetric apparatus.

3. Results and discussions

3.1. Consistency and setting time of fresh pastes

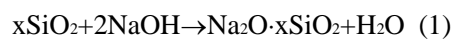
Results of the consistency tests are shown in Table 3. The geopolymer with 100 % MK had 20 cm penetration and all the samples containing RHA had 40 cm which is the maximum penetration. The mixture having only MK is less consistent than those having RHA blends. Even in small proportion, the presence of RHA had a dilute effect and improved the workability of the mixture at constant liquid/solid ratio, showing prospect of good workability at lower liquid/solid ratios.

From setting test results (Fig. 1) binders having respectively 0, 12.5, 25 and 50 % RHA presented respectively 128, 144, 140 and 290 minutes as initial setting time. The final setting time of binders with 0 to 25 % RHA as replacement is at 230 minutes while that of the sample having 50 % RHA is at 450 minutes. The presence of RHA in pastes in proportions up to 25% resulted a little increase in setting time (12 -16 min.) compared to the pastes having 100 % MK. The initial and final setting times shown by pastes having up to 25 % RHA are almost similar to that of ordinary Portland cement [36]. Rice husk Ash in pastes acted as setting retarder. The increase in setting time is not significantly perceptible for blends proportions up to 25 %. At 50 % RHA in pastes, the initial setting time was extended by 162 minutes compared to the reference sample. According to Sazmal et al. [37], this behavior of pastes having 50% RHA is due to high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the mixture which inhibited the geopolymerization reaction by the precipitation of Si-Al phases which avoided contact between the reactive material and the activation solution. The paste takes longer curing time to harden that is the reason why reduction in the setting performance and extension in setting time are observed. With pastes having up to 25% of RHA, there is also increase in $\text{SiO}_2/\text{Al}_2\text{O}_2$ ratio, but it is not enough to hinder significantly the geopolymerization process.

3.2. Tensile strength of hardened pastes

The tensile strength is determined in order to get some idea of the cohesion between the particles and the evolution of chemical bonds. It provides data on the integrity and safety of materials, components and products, helping manufacturers to ensure that their finished products are fit-for-purpose and manufactured to the highest quality. From the result shown in Figures 2, it is observed that the presence of RHA in the mixture has an effect both on maximum stresses and the elongations of samples before rupture. At 7 days of curing, the maximum tensile stresses of samples before rupture are respectively 1.39; 0.64; 0.94; 0.50

MPa for samples having 0, 12.5, 25 and 50 % RHA as partial replacement of MK. The corresponding elongations of the same samples at their maximum tensile stresses are respectively 3.03; 1.94; 1.87 and 2.01 mm. The samples with MK partially substituted with RHA exhibited increase in tensile strength for 12.5% and 25% replacement of MK by RHA, then the strength decreases at 50 %, but all maximum stresses are less than that of the reference sample with 0% replacement. The reverse situation is observed in the case of elongations of samples before ruptures. It decreases from 12.5 % to 25 % replacements of MK with RHA and increases at 50 % with the reference sample having the highest elongation. At 28 days, maximum tensile stresses are respectively 0.94; 1.91; 1.18 and 0.92 MPa for 0, 12.5, 25 and 50 % replacement of MK by RHA, while elongations of these samples are respectively 1.66; 2.44; 1.91; and 2.01 mm. At 28 days of curing, samples with MK partially replaced by RHA elongated more than the sample having only MK showing the benefit of RHA to the elastic deformation of geopolymers. This behavior can be attributed to the un-reacted silicate gel from the reaction of excess of RHA and NaOH by equation (1) [38] remained in samples which can weaken their strength if it in excess but makes the sample to have higher extension capacity before rupture. The tendency of samples containing RHA to more deform than to exhibit the brittleness behavior makes the material good in non-structural applications [39].



Compared to the reference sample (with 0% RHA), the sample with 12.5 RHA exhibited increase in tensile strength which is even higher than all other mixtures. As the replacement of RHA increased, a gradual decrease in strength is observed, but samples with RHA showed increase in strength from 7 days to 28 days of curing while the reference

sample having only MK as aluminosilicate showed decrease in strength. The sample having only MK as alumino silicate was also the most fragile or brittle one with the lowest stress and elongation before the rupture. This deterioration in strength of MK geopolymers in long durations of curing was observed previously by Claudio Ferone et al [40]. They attributed that phenomenon to the shrinkage that causes micro-fractures of the material and reduction of strength. They also showed that curing of metakaolin based geopolymers at ambient temperature is critical because of a substantial material shrinkage related to the amount of evaporable water which was found to increase with Si/Al ratio of the geopolymer mixture. Si/Al ratio of 1.75 was chosen as the best compromise between mechanical performances and shrinkage. With the present results the partial replacement of up to 50 % replacement of MK by RHA reduced the negative effect of drying shrinkage on mechanical properties. Except samples having 12.5 and 25 % RHA that have shown increase in elongations from 7 to 28 days of curing, the other samples exhibited decrease in that property. Despite the fact that they used a mixture of sodium hydroxide and sodium silicate, Borges et al [39] obtained almost similar results by observing the benefit of up to 30 % rice husk ash on flexural and compressive strengths of 0 % to 60 % blends of metakaolin with rice husk ash. The drop in strength could also be explained by the reduction of the amount of the geopolymer binding phases in the mixture, the negative effect of unreacted silica or alumina, the presence of air voids and excess gel [39, 41]. Since the rate of dissolution of SiO_2 in RHA is lower than the one in MK, the matrix formation takes place without total reaction of amorphous SiO_2 from RHA when it is added in proportions more than 30% of MK, yielding un-reacted materials as fillers that reduce the strength of products [39].

3.3. Microstructure of hardened pastes

The micrographs of hardened geopolymers (Fig. 3 and 4) showed typical microstructure of metakaolin based geopolymer cement (Fig. 3a). At low magnification,

voids due to air bubbles that characterize the geopolymerization of MK are visible. At higher magnification, globular type grains of polysialates with nanometric size are observed (circled in Fig. 3a) in a matrix where porosity of similar size seems intrinsic to the product. The size of microcracks is important. Kamseu et al. [42] indicated that those micro-cracks also called wing cracks propagate into the matrix easily due to the fact that the crosslinking between the nanometric grains of polysialate is poor. The higher the alumina oligomers is, the important is the extension of the micro-cracks as those oligomers are at the origin of the development of poor bonds and crosslinking within the phases of the matrix. The addition of silica from RHA has primary impact on the reduction of the size of air bubbles and the improvement of the densification of the matrix (Fig. 3d and Fig. 4a). Rice Husk Ash in alkaline solution generates additional soluble silica which increased the overall Si/Al ratio of samples as indicated in their spots atomic composition estimation by EDX (Table 4). Slight decrease in silica content between G0 and G12.5 can be due to homogenization of the mixture. Several authors previously reported that there is a strong correlation between the Si/Al ratio of metakaolin geopolymers and mechanical properties [43]. The increase in Si/Al ratio decrease Si-O-Al bonds and increases Si-O-Si bonds in the geopolymer gel which are responsible to the increase of mechanical strength. Si/Al ratios lower than 1.40, yielded to geopolymers with high porous matrix that contributed to reduce the strength of the resulting product. They observed optimum gain in strength with Si/Al ratio between 1.40 and 2. In samples having RHA blends, the polysialates structure moves from simple sialates in the case of metakaolin without RHA blend to polysialate disilixos and even multisilixos when Si/Al is greater than 2. Extent of crosslinking allows long chains of aluminosilicates to be formed with the consequence in significant reduction of air voids bubbles and volumes of larger capillary pores [42, 44]. These observations explain the progressive increase in tensile strength with the increase proportions of RHA in MK with G12.5 and G25 which were less affected by the

micro-cracks network. However, the addition of 50 % in weight of RHA caused the decrease in the densification as it can be observed at high magnification (Fig. 4e) which is in accordance with the decrease in tensile strength for this mixture. This reduction in strength could also be due to the decrease of the fraction of silicates that effectively participated in the geopolymerization reaction and significant presence of unreacted species (pointed in Fig. 4e). Blends of metakaolin with less than 25 % of RHA can contribute to reduce the negative effects of micro-cracks network in metakaolin geopolymers.

3.4. Thermogravimetric analysis of hardened pastes

The weight loss in geopolymer is generally attributed to the loss in water in samples [43]. The tested samples in Figure 5 exhibited a significant difference in their weight loss confirming previous results that stated that the water content in geopolymers depends on their Si/Al ratio which is maximized at about 1.96 [44]. The sharp weight loss in samples at about 170 °C which is almost similar in all samples ($\approx 4\%$) can be attributed evaporable water. For temperatures between 170 °C and 350 °C, the weight loss is due to the water tightly bound in the geopolymer gel as the result of the polycondensation reactions [43]. Samples with 12.5 and 25 % RHA exhibited higher weight loss in that temperature interval compared to the reference sample (G0). The lower mechanical performance of sample G50 having an excess of RHA that leads to higher Si/Al ratio is confirmed by the lower weight loss of that sample. The high Si/Al (> 1.96) ratio of G50 is not favorable to its complete geopolymerisation therefore leading to less water content in its gel and to the presence of unreacted species that reduced the strength. The weight loss at temperature higher than 350 °C for samples G12.5 and G25 could be due to loss of the water caused by the condensation of silanol and aluminol groups (dehydroxilation) at the surface of geopolymers [44].

Conclusions

Performance of geopolymers made with MK partially replaced with RHA and 10 M sodium hydroxide solution were studied in the present study. From the investigations carried out, the following conclusions can be drawn:

- The presence of RHA as partial replacement of MK in geopolymer pastes has a dilute effect with beneficial consequence on the improved of the workability of the pastes as evidenced by decrease in consistency of pastes containing RHA;
- Rice husk Ash in pastes acted as setting retarder. The increase in setting time is not significantly perceptible for blend proportions up to 25 %.
- The samples with MK partially substituted with RHA exhibited increase in tensile strength for 12.5% and 25% replacement of MK by RHA;
- The negative effect of reduction in strength with time due to micro-cracks was eliminated for mixture having up to 50 % RHA as partial replacement of MK;
- From microstructure examinations, the addition of silica from RHA had primary impact on the reduction of the size of pores due to air bubbles and the improvement of the densification of the matrix with beneficial performances in tensile strength.

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