



The Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratios on the Properties of Geopolymers Prepared from Water Treatment Residue (WTR) in the Presence of Heavy Metals

N. Waijarean, S. Asavapisit, K. Sombatsompop, and K.J.D. MacKenzie

Abstract— The aim of this research was to develop a solidification binder using water treatment residue (WTR) as the aluminosilicate source and black rice husk ash (BHA) as a source of silica. The binder was prepared to obtain $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 1.78 and 2.00 and was activated with NaOH using $\text{Na}_2\text{O}/\text{SiO}_2$ equals to 0.25. Electroplating sludge (EPS) were added to the binders at 30, 50 and 70% by weight. The geopolymer synthesized with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.00 gave higher strength than that at 1.78 at all curing duration. The addition of EPS at increasing amounts resulted in a reduction of strength. XRD revealed the presence of sodium aluminium silicate hydrate, and sodium zinc silicate, sodium iron silicate oxide and sodium aluminum hydroxide chromium oxide in geopolymer matrices, while an FTIR vibration band related to the geopolymer product shifted to 1002 cm^{-1} .

Keywords— Black rice husk ash, Geopolymer, Water treatment residue, Strength, XRD, FTIR

1. INTRODUCTION

Geopolymers (GPs) are inorganic materials that can be synthesized from a variety of industrial by-products and wastes, including sludge from water treatment plants, blast furnace slag, coal fly ash, mining waste and steel slag. They are formed by alkaline activation with controlled water content and suitable molar compositions [1]. The Si/Al ratios of the starting material play a key role in geopolymerization process and the geopolymer properties. MacKenzie et al. (2007) have reported that optimal properties of the products are achieved with the molar ratios in the range $\text{SiO}_2/\text{Al}_2\text{O}_3 < 3.3$, $\text{H}_2\text{O}/\text{Na}_2\text{O} < 10$ and $\text{Na}_2\text{O}/\text{SiO}_2 < 0.3$ [2-4]. Geopolymer technology is useful for utilization of wastes streams to produce materials that are more environmentally-friendly than ordinary Portland cement (OPC), and have a number of other applications such as the immobilization of toxic and radioactive wastes, or thermal insulation of buildings [5].

Water treatment residue (WTR) is a waste product from water treatment plants. It contains high proportion of clay minerals, principally kaolinite, in addition to aluminium and iron salts. Two hundred tons of WTR are

generated per day and disposed of directly into landfills. Due to the high cost of disposal process, reuse of WTR for the manufacturing of ceramics and bricks has been considered as an alternative to dumping in landfills. Its major chemical components especially silicon and aluminum could make WTR a suitable raw material for geopolymer production [6].

Rice husk is a by-product available in rice-producing countries. It is widely used as a biomass fuel in rice mills and electricity power plants by burning the husks under controlled conditions [1-2]. Such combustion processes produce on average about 18% rice husk ash (RHA), either as black husk ash (BHA) with a high carbon or white husk ash with a low carbon. BHA consists of highly crystalline silica with a very large specific surface area (about $50\text{-}100\text{ m}^2/\text{g}$) [7]. RHA is a well-known pozzolan that can be used in building materials and other applications such as insulation material, a fuel supplement in the manufacture of OPC and fertilizer.

Previous research has focused principally on the production of geopolymers from raw materials such as coal fly ash, clay minerals, and blast furnace slag [1-2, 6-8]. Very little work has been done on the use of WTR as the aluminosilicate source, with the Si/Al ratios adjusted with BHA. The goal of this research is to utilise two waste materials, WTR and BHA to develop a new cementing material with a potential application to immobilize heavy metals from an electroplating industry. The geopolymers under development would provide an environmentally-friendly approach to waste management by reducing the amount of waste disposed of in landfills.

2. EXPERIMENTAL PROCEDURE

Materials

The water treatment residue (WTR) is waste product obtained from a water treatment plant at Bangkaen, Bangkok Province, Thailand. WTR was thermally activated by calcining in an electric furnace at $800\text{ }^\circ\text{C}$ for 1 hour, and then ground to be retained on sieve no. 325.

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(45 μ m). The chemical composition of the WTR calcined at 800 °C determined by XRF is presented in Table 1. SiO₂ and Al₂O₃, were present in WTR at 54.00 and 30.40 %wt., respectively, with an initial ratio between SiO₂ and Al₂O₃ of 1.78. The crystalline phases of WTR calcined at 800 °C were determined by XRD to be quartz (JCPDF no. 03-065-0466) and mica (JCPDF no. 03-065-0466) (Fig. 1).

The black rice husk ash (BHA) used was a by-product from controlled burning of rice husks from a dried paddy factory in Nakompratom Province, Thailand. The rice husk was fired in a cyclonic furnace under controlled temperature above 850 °C for 1 hour to remove carbon and volatile organic compounds. The as-received BHA was ground in a Los Angeles abrasion machine for 6 hours to gain a particle size retained on a 45 μ m mesh by wet-sieved less than 34%. The chemical composition of BHA determined by XRF is shown in Table 1. The high silica content (over 90% wt.dry) suggests that BHA

could be a good silicate source. XRD showed an amorphous phase of SiO₂ in cristobalite (JCPDF file no. 04-007-4907), in addition to some phosphide oxide (P₂O₅: JCPDF file no. 04-007-2296) (Fig. 1).

Electroplating Sludge (EPS) was brought from the electroplating facility located at Nongkham, Bangkok Province, Thailand. The EPS was generated from the waste water treatment plant by adjusting the pH of the wastewater to transform the soluble metals into metal hydroxide, followed by dewatering of the sludge. EPS was dried before reducing to a particle size less than 50 μ m. The concentration of heavy metals in EPS was measured by atomic absorption spectrophotometry (AA-6300 series no. A305246). Zinc, iron and chromium were found to be the major metals present at 216.45, 81.8, and 22.40 mg/kg dry sludge, respectively.

Table 1: The chemical compositions of WTR and BHA

Content (wt% dry)	Elements as an oxide										%MC	%LOI	SiO ₂ /Al ₂ O ₃ ratio
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	CaO	MgO	TiO ₂	SO ₃	Na ₂ O	MnO			
WTR*	53.90	30.40	9.18	2.42	0.93	1.01	0.85	0.39	0.24	0.18	0.41	1.86	1.78
BHA	94.00	0.16	0.13	3.38	0.77	0.32	0.01	0.14	0.04	0.13	2.50	7.00	-

WTR* = WTR calcined at 800°C

%MC = % moisture content

% LOI= %Loss on ignition at 950°C

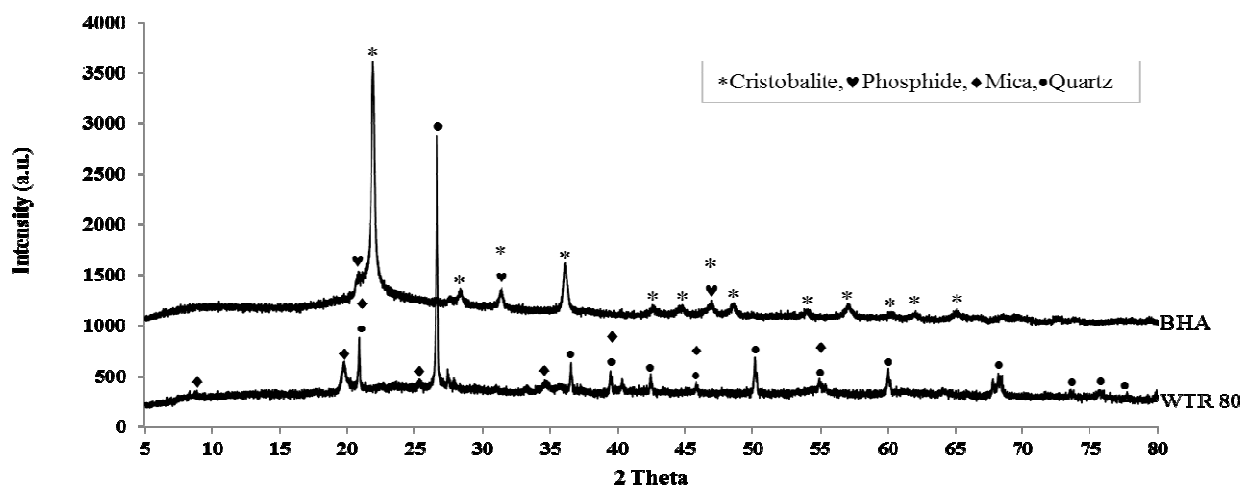


Fig. 1 XRD patterns of BHA and WTR

Geopolymer synthesis

The geopolymer were synthesized from calcined WTR. The molar ratio between SiO₂ and Al₂O₃ of WTR was adjusted from an initial ratio of 1.78 to 2.00 using BHA. EPS was added to the binders at the levels of 0, 30, 50 and 70% by weight. The proportions of each mixture are shown in Table 2. The water content of each mixture was determined by ASTM C187-68 [9]. NaOH was dissolved in the water before adding to the solid mixtures and mixed for 15 min. The homogenised mixtures were

transferred into cylindrical PVC molds, and shaken for 5 min to remove air bubbles. The samples were demolded after 24h, wrapped with cling film to prevent the loss of water from the mixture and allowed to cure at an ambient temperature of 29 \pm 2°C.

Compressive strength test

The cylindrical samples with an average diameter of 35 mm and height of 70 mm were determined by ASTM C39. The compressive strength was measured after curing for 7, 28, 42, and 60 days. Six replicates of each

sample were measured, to give a standard deviation in the range of ± 0.5 . The surfaces of all samples were flat and parallel. A fragment of the GPs after testing was retained for microstructural analysis.

Microstructural characterizations

The GPs samples were analysed using XRD, FTIR and SEM to study the mechanism of geopolymerization after curing for 28 days. Dried-powder of each sample was analysed under following conditions

1. The crystalline phases were examined by XRD (PAN alytical series X'Pert PRO) with a graphite monochromator and $\text{CuK}\alpha$ radiation source. The sample was scanned from 4 to $80^\circ 2\theta$ at a rate of $0.04^\circ 2\theta$ step, at a counting time of 0.4s per step.
2. The functional groups of the GP were studied using FTIR spectroscopy (Perkin-Elmer, version 2000). The spectral data were collected in the range between 400 and $4,000\text{ cm}^{-1}$.
3. The morphology characterization of the products were studied by SEM (JEOL JSM-6610LA) at 15 kV. All samples were coated with carbon.

3. RESULTS AND DISCUSSION

3.1 Effect of EPS on strength of WTR-based geopolymer

The strength development of WTR-based geopolymers with and without EPS is shown in Fig 2. The synthetic geopolymer prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 2.00 gave strength higher compared to those with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

of 1.78 at all curing time. It is generally known that at higher or lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio exhibits reduced strength due to the amount of unreacted SiO_2 or Al_2O_3 remaining in the sample [10]. Addition of EPS at increasing amount from 30 up to 70% wt causes a reduction of strength of geopolymer. The incorporation of a higher amount of EPS was associated with a decrement of the raw materials (WTR and BHA) for geopolymerization. Strength gain was caused by the dissolution of Si and Al from the aluminosilicate structure present in the WTR under highly alkaline conditions, resulting in a negative charge imbalance of the 4-coordinated Al; this imbalance was compensated by Na^+ from NaOH, which led to the formation of aluminosilicate network [11].

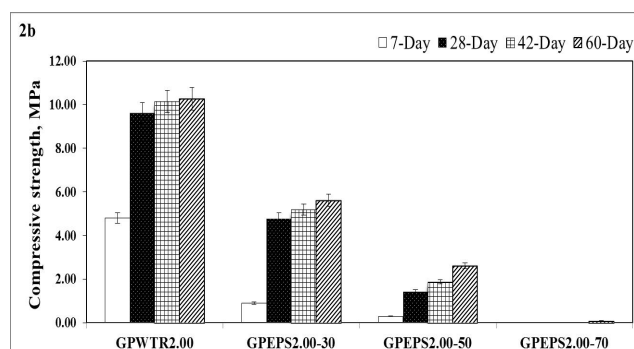


Fig. 2. Compressive strength of synthetic geopolymer incorporating various amounts of EPS; (a) without BHA and, (b) with BHA

Table 2: Proportions of geopolymer mixtures

Sample ID	Binders (%wt. dry)			Activator NaOH (gram)	Molar Ratios		H ₂ O
	WTR	BHA	EPS		Na ₂ O:SiO ₂	SiO ₂ /Al ₂ O ₃	
GPWTR1.78	700	0	0	121.25	0.25	1.78	364
GPEPS1.78-30	490	0	210	84.87	0.25	1.78	273
GPEPS1.78-50	350	0	350	60.62	0.25	1.78	217
GPEPS1.78-70	210	0	490	36.38	0.25	1.78	213
GPWTR2.00	655	45	0	127.15	0.25	2.00	357
GPEPS2.00-30	458	32	210	89.00	0.25	2.00	266
GPEPS2.00-50	327	23	350	63.57	0.25	2.00	224
GPEPS2.00-70	196	14	490	38.14	0.25	2.00	215

3.2 Effect of EPS on microstructure of WTR-based geopolymer

XRD

Fig 3 shows the XRD patterns of geopolymers synthesized from WTR and BHA with different amounts of EPS at the age of 28 days. The peak of quartz (PDF no. 03-065-0466) is clearly presented as an unreacted component in all samples, while silicon oxide as cristobalite phase (PDF no. 04-008-7827) is only present in the geopolymer with a $\text{Si}_2\text{O}/\text{Al}_2\text{O}_3$ of 2.00, both with

and without EPS. The crystalline phase of muscovite (PDF no. 04-011-5121), vermiculite (PDF no. 00-060-0340), and aluminum silicate oxide (PDF no. 01-074-1976) are observed in the geopolymer product. It is possible that these aluminosilicate clay minerals are inactive for geopolymerization reaction. The apparent phase of sodium aluminum silicate hydrate (NASH: PDF no. 04-014-2162) through faujasite (PDF no. 00-012-0246) in geopolymer product, indicating that the reaction between NaOH activator and aluminosilicate material under this condition occurred.

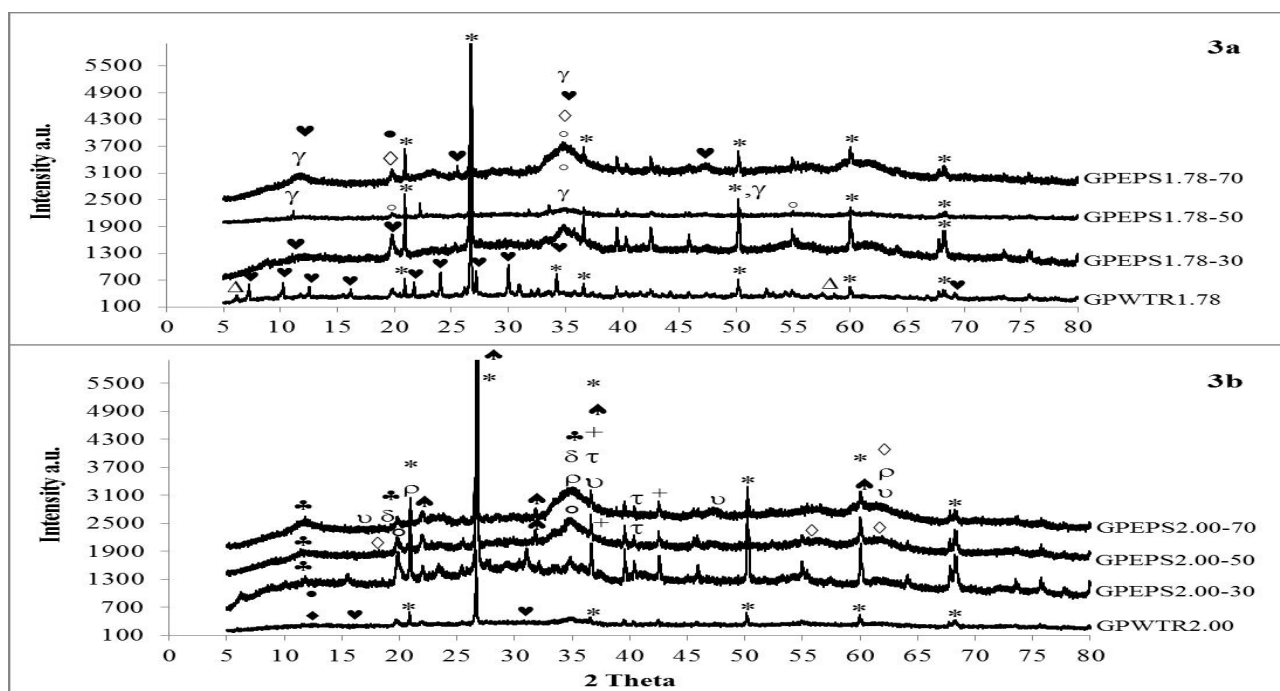


Fig. 3. XRD patterns of 28-day geopolymers incorporating various amounts of EPS; (3a) without BHA and (3b) with BHA. Key: *= quartz, •= aluminium silicate oxide, ♥= NASH, ♦= faujasite, Δ= vermiculite, ♠= cristobalite, °= sodium zinc silicate, ♣= Muscovite, += iron oxide, ◇= sodium iron silicate oxide, τ= zinc oxide, δ= sodium silicate oxide, ρ= sodium zinc silicate oxide, υ=sodium aluminum hydroxide chromium oxide, γ= sodium aluminium iron hydrate silicate.

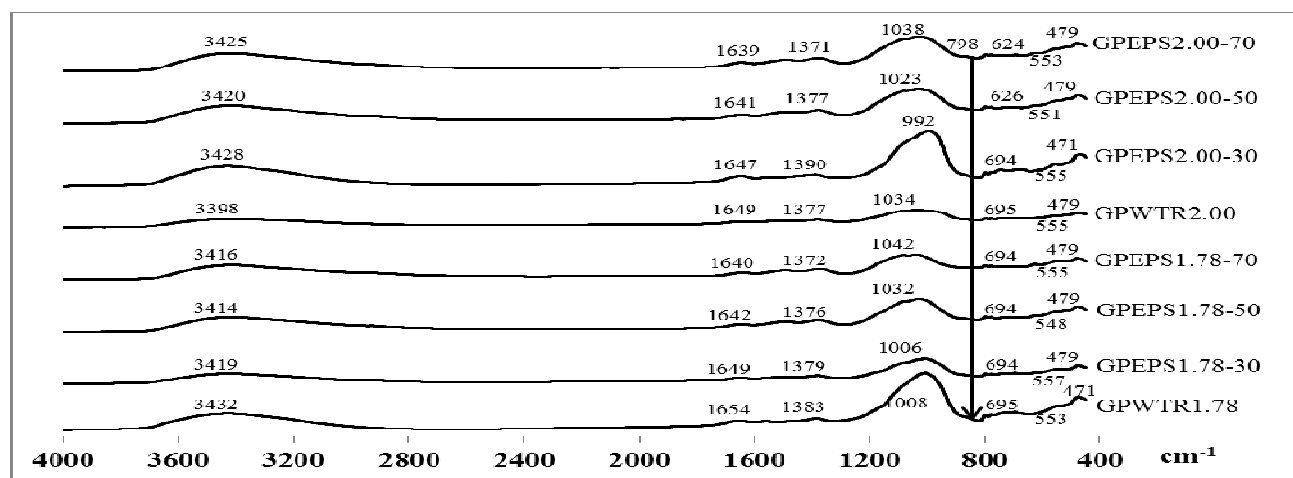


Fig 4 FTIR spectra of geopolymer synthesized with and without EPS

Table 3: EDS results of 28-day WTR-based geopolymer synthesized with 50% heavy metal waste.

Sample	% Mass of elements															
	Si	Al	Na	Zn	Fe	Cr	K	Mg	Ca	Ti	P	S	Cl	O	C	Total
GPEPS 1.78-50%	17.16	12.29	7.50	7.59	6.54	1.79	1.91	0.47	1.16	0.37	0.63	1.28	1.30	21.56	18.46	100

Other crystalline phases in the geopolymer products synthesized with EPS include sodium zinc silicate (PDF no. 00-030-1267), iron oxide (PDF no. 00-001-1223), sodium iron silicate oxide (PDF no. 04-002-8286), zinc oxide (PDF no. 04-014-0085), sodium zinc silicate oxide (PDF no. 00-019-1262), sodium aluminum hydroxide chromium oxide (PDF no. 01-077-0064), and sodium aluminium iron hydrate silicate (PDF no. 01-083-2369). These are indicative of insoluble forms of a heavy metal

waste incorporating into the aluminosilicate structure, implying that it is possible for these heavy metals to be immobilized in WTR- based geopolymer matrices [8, 12, 13].

FTIR

Fig 4 shows the FTIR spectra of geopolymer with and without EPS, which was reported in the wavenumber regions between 4000 and 400 cm^{-1} . The center of a

vibration band of all samples was shown dominantly in regions around 1000 cm^{-1} assigned to Si-O-T (T= tetrahedral Al or Si) due to associated solidification of geopolymer product [1]. The vibration bands at 3398 cm^{-1} and $1639\text{ to }1654\text{ cm}^{-1}$ were observed to correspond to the water molecule and the OH group, respectively [1, 8, 14-15]. Other bands at about 798 cm^{-1} indicate the presence of Si-O-Si and symmetric and asymmetric stretching of tetrahedral AlO_2 and SiO_4 units in the geopolymers [8].

SEM-EDS

The morphology characterization of the geopolymer product synthesized without BHA and with 50% EPS is shown in Fig 5. The inhomogeneity on the surface area after reaction with NaOH solution and curing for 28 days was observed. This is revealed in some areas of insoluble iron, zinc and chromium ion as determined by EDS analysis, which through XRD analysis was shown to be composed of a heavy metal hydroxide form. The heavy metal ions were retained in the geopolymer product with the percent mass of zinc, iron and chromium, which are reported in Table 3. It can be seen that the heavy metals were incorporated in the aluminosilicate structure, but the bonds on Al and Si tetrahedral building blocks in geopolymer were also unaffected. It may be cause due to the strength development in geopolymer matrix during geopolymerization [8, 11, 16-17].

4. CONCLUSIONS

This study indicates that the waste residues, WTR and BHA, are suitable raw materials for geopolymer synthesis, and is applicable to immobilize heavy metals from electroplating industry. The sample with Si/Al ratio of 2.00 without EPS and with 30% EPS were found to produce the greatest strength at all curing times. The reaction products identified by XRD including sodium aluminum silicate hydrate, sodium zinc silicate, sodium iron silicate oxide, sodium zinc silicate oxide, sodium aluminum hydroxide chromium oxide, and sodium aluminium iron hydrate silicate. GPs formation was confirmed by FTIR at the vibration band about 1000 cm^{-1} . SEM image shows the inhomogeneity on the surface of geopolymer synthesized from WTR with 50% EPS at the age of 28 days, which revealed retention of insoluble heavy mealtals in accordance with EDS analysis.

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