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Strength and microstructure of water treatment residue-based geopolymers containing heavy metals

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HIGHLIGHTS

- New cementing materials from water treatment residue was developed.
- WTR can be used to produce geopolymer for containing heavy metals.
- Using WTR is an environmental friendly approach for waste management.

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ABSTRACT

This research investigated the use of water treatment residue (WTR) as an alumino-siliceous material from which to synthesize geopolymers. WTR with an initial SiO_2:Al_2O_3 ratio of 1.78 was pretreated by calcining at temperatures of 600, 800 and 900 °C for 1 h. NaOH was reacted with WTR at an Na_2O:SiO_2 ratio of 0.25. Without thermal treatment of the WTR, XRD showed that dehydroxylation of the halloysite did not occur, and thus, no strength was gained during the early stages. Samples prepared from WTR calcined at 800 °C exhibited the highest strength at all curing times. FTIR spectra revealed that the major asymmetric vibration band shifted at 1000 cm^{-1}, corresponding to the hydration products. When plating sludge was added at 50 wt%, the strength gained by the sample after 28 days was only 34% of the control sample prepared from WTR calcined at 800 °C.

1. Introduction

Water treatment residue is generated from the water treatment process. The various water treatment processes include coagulation, sedimentation and sand filtration and are used to remove organic matter and suspended solids from surface water. The coagulating agents used for water treatment consist of aluminum and iron salts, as well as organic polymers. The major chemical components of water treatment residue are silica and alumina. An increasing amount of water treatment residue is generated each year due to the growing demand on the water supply. These water treatment residues are currently disposed of in landfills. Due to the cost of land disposal, reusing water treatment residues to manufacture ceramics and bricks has been considered as an alternative to landfills [6,20,22].

Geopolymers are alkali-activated aluminosilicates that are amorphous to semi-crystalline three-dimensional aluminosilicate networks. Geopolymers can be synthesized from a variety of industrial by-products and wastes, such as thermally activated clays, blast furnace slag, coal fly ash, zeolites, kaolin, metakaolin and steel slag, all of which can react with alkali solutions to produce a hardened material [13]. Due to the wide range of available raw materials, a broad range of Si/Al ratios are observed. The influence of the Si/Al ratio on the formation and compositional variability of aluminosilicate gels has been investigated [5,11,19]. An increase in the SiO_2/Al_2O_3 ratio of the initial mixture increases the setting time and strength of the product [10,11,21].

Several research papers have reported on the use of geopolymer technology for the stabilization and solidification of hazardous metals. Examples of wastes that have been encapsulated within

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geopolymer matrices include contaminated soils from mine tailings, radioactive wastes, and electric arc furnace dust [1,8,16]. Geopolymers are used as binders to replace traditional hydraulic binders. Wastes are believed to be either physically or chemically encapsulated within the three-dimensional alumino-silicate networks [17,23]. Industrial wastes contaminated with hazardous metals, such as Pb, Cd, Cr or Zn, and solidified using different geopolymer reagents, such as sodium hydroxide, potassium hydroxide, sodium silicate, potassium silicate, kaolinite, metakaolinite, blast furnace slag and lignite fly ash, have been studied [18,30].

The effects of the alkaline dosage and Si/Al ratio on the immobilization of heavy metals in municipal solid waste incineration fly ash-based geopolymers have been explored [24]. A geopolymer with the highest strength was obtained at an intermediate alkaline activator dosage (Na/MSWI fly ash = 2.8 mol/kg) and Si/Al ratio (Si/Al molar ratio = 2.0). Higher alkaline activator dosages enhanced the structural disruption of the original aluminosilicate phases and produced a higher degree of polymerization of the geopolymer networks. At a low Si/Al ratio, an increasing amount of tetrahedral Al was incorporated into the silicate backbone. As the Na/MSWI fly ash ratio increased, the microstructure changed from large macropores to more mesopores and micropores. The pore volume distribution of the geopolymers shifted to larger pores as the Si/Al ratio increased. The lowest leachable fraction of Cr, Cu and Zn was obtained using an intermediate alkaline dosage. The leachable fraction of Cr and Cu decreased as the Si/Al ratio increased, while Zn reached its lowest point at an intermediate Si/Al ratio.

Previous research has focused on the use of geopolymers derived from waste materials, such as coal fly ash and blast furnace slag [19,27,26]. Very few research efforts have focused on the use of water treatment residue (WTR) as a waste-immobilizing agent. The goal of this research was to develop new cementing materials from WTR because of its suitable chemical composition. Using WTR is an environmentally friendly approach for waste management, for example, immobilization of plating sludge containing heavy metals, thus reducing the amount of waste going to the landfill. In this work, the optimum calcining temperature for preparing WTR was investigated between 600 and 900 °C for 1 h, and the geopolymerization reaction between WTR and NaOH with and without plating sludge was evaluated by determining the geopolymer strength and characterizing the microstructure using various techniques including XRD, FTIR and SEM.

2. Experimental procedure

2.1. Materials

The water treatment residue, which was obtained from a water treatment plant at Bangkaen in Bangkok Province, Thailand, was pre-treated by calcining the residue in an electric furnace at temperatures of 600, 800 and 900 °C for 1 h. After calcining, the residue was ground to obtain a particle size of which was retained on sieve No. 325 (45 μm). The ground residue was analyzed by X-ray fluorescence (XRF), and the oxide content is reported in Table 1. The crystalline phases present in calcined and non-calcined WTR were examined by X-ray diffraction (XRD), and the results are shown in Fig. 1(a,b).

Electroplating sludge (EPS) was brought from the wastewater treatment plant of an electroplating facility located at Nongkham in Bangkok Province, Thailand. The plating sludge was obtained by adjusting the pH of the wastewater to between 7.5 and 8 to transform the soluble metals into metal hydroxides. The less soluble metal hydroxides were removed and dewatered. The sludge was then oven-dried before the particle size was reduced to less than 50 mm. The ground sludge was subjected to microwave digestion, and the concentration of heavy metals present in the sludge was measured by atomic absorption spectrophotometry (AA-6300 series No. A305246). Zn, Fe and Cr were the major metals present in EPS at 216.45, 81.18 and 22.40 mg/kg dry sludge, respectively.

2.2. Geopolymer synthesis

Geopolymer was synthesized from calcined WTR with an initial SiO_2:Al_2O_3 ratio of 1.78. Analytical-grade NaOH solution from Merck was reacted with calcined and non-calcined WTR at an Na_2O:Si_2O ratio of 0.25. The proportion of each mixture is shown in Table 2. The water used for each mixture was determined using ASTM Method C 187-68 [2]. NaOH was dissolved in the water mixture and then added to the solid mixture and mixed for 15 min to homogenize the sample. The mixtures were then transferred to cylindrical PVC molds (diameter 35 mm, height 70 mm), and vibrated for 2 min to remove entrapped air bubbles. The samples were demolded after 24 h, wrapped with cling film to prevent the loss of water and allowed to cure at an ambient temperature of 28 ± 2 °C. The development of strength and the characteristics of the microstructure were used to understand the geopolymerization reaction between the WTR and NaOH. The optimum calcining temperature of the WTR was determined according to the development of strength in the specimens and was used to prepare WTR for further study of metal immobilization. EPS was added to the binders (WTR and NaOH) at 0%, 30%, and 50% by weight.

Table 1
Chemical composition (wt%) of raw materials.

Element as an oxide	Content (wt%) of WTR	
	110 °C	800 °C 1 h
SiO_2	54.00	53.70
Al_2O_3	29.30	30.10
Fe_2O_3	9.84	9.56
K_2O	2.58	2.49
CaO	1.01	0.98
MgO	0.97	1.00
TiO_2	0.91	0.87
SO_3	0.43	0.38
P_2O_5	0.35	0.35
MnO	0.19	0.18
Si_2O/Al_2O_3 molar ratio	1.84	1.78

2.3. Compressive strength test

After aging for 7, 14, 28 and 60 days, the cylindrical specimens were subjected to a compaction test according to the ASTM C39 standard. The unconfined compressive strength (UCS) results for each of six samples were averaged, and the standard deviation was in the range of ±0.5. The strength of the samples containing EPS was measured after curing for 14 days.

2.4. Microstructure characterization

The crystalline phases of the samples with and without EPS were examined using X-ray diffraction (XRD). A Bruker AXS series D8 Discover with Cu K radiation with an average wavelength of 1.54184° was used. The powder sample was scanned at a rate of 0.4 s per step. The XRD patterns of the control geopolymer (without EPS) and the geopolymer containing 50 wt% EPS are shown in Fig. 1(c,d). The morphology was characterized with scanning electron microscopy (SEM) using, a JEOL series JSM-6400. All of the samples prepared for SEM analysis were coated with gold. The functional groups of the synthesized geopolymers with and without EPS were studied using Fourier transform infrared (FTIR) spectroscopy. A powder sample with a small amount of KBr was pressed in a mold and then introduced into a PerkinElmer FTIR, version 5.3.1. The spectral data of the sample were collected between 400 and 4000 cm^{-1}, and the FTIR spectra are shown in Fig. 2(a–d).

3. Results and discussion

3.1. Effect of calcining temperatures on properties of WTR

The oxide content of non-calcined WTR (oven-dried at 110 °C for 24 h) and calcined WTR dried at 800 °C for 1 h are shown in Table 1. SiO_2, Al_2O_3 and Fe_2O_3 were the main oxides present in WTR. The molar ratios of SiO_2/Al_2O_3 present in non-calcined and calcined WTR were 1.84 and 1.78. The X-ray diffraction patterns of non-calcined WTR and WTR calcined at a temperature of 800 °C are shown in Fig. 1a and b. The peaks of halloysite ($Al_2Si_2O_5(OH)_4$), muscovite ($KAl_3Si_3O_{10}(OH)_2$), quartz (SiO_2) and anatase (TiO_2) appeared in the XRD pattern of non-calcined WTR (Fig. 1a). When WTR was calcined at 800 °C, the halloysite peak was not observed (Fig. 1b). Either pretreatment at a temperature of 550 °C or grinding for at least 15 min could induce dehydroxylation; destruction of the 1:1 layer-lattice aluminosilicate structure, which resembled kaolinite; and conversion of the octahedral aluminum to 4- and 5-fold coordinated aluminum [9,15]. FTIR spectra