Construction and Building Materials 88 (2015) 74–83

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of solid-to-liquid ratios on the properties of waste catalyst–metakaolin based geopolymers

Hui Cheng [a], Kae-Long Lin [b,*], Rong Cui [a], Chao-Lung Hwang [c], Ta-Wui Cheng [d], Yu-Min Chang [e]

[a] *School of Environment and Materials Engineering, Yantai University, China*
[b] *Department of Environmental Engineering, National ILan University, Taiwan*
[c] *Department of Construction Engineering, National Taiwan University of Science and Technology, Taiwan*
[d] *Department of Mineral Resources Engineering, National Taipei University of Technology, Taiwan*
[e] *Graduate Institute of Environmental Engineering and Management, National Taipei University of Technology, Taiwan*

HIGHLIGHTS

- WCMBG samples contained 10% waste catalyst exhibited greater compressive strength and lower porosity.
- Geopolymer samples were filled the pores, thus leading to the formation of a denser structure.
- WCMBG samples showed the major structures of the Si and Al are Q^4(3Al) and Q^4(2Al).
- The porosity of a WCMBG increases with the level of waste catalyst replacement.
- We report effect of solid-to-liquid ratios of waste catalyst–metakaolin based geopolymers.

ARTICLE INFO

Article history:
Received 28 July 2014
Received in revised form 1 December 2014
Accepted 2 January 2015
Available online 22 April 2015

Keywords:
Metakaolin
Geopolymer
Solid-to-liquid ratio
Waste catalyst
Microstructural

ABSTRACT

In this study, the changes caused by adding a waste catalyst on the properties of the final product were investigated by applying curing on samples of waste catalyst metakaolin-based geopolymers (WCMBGs) prepared with different solid-to-liquid (S/L) ratios (0.66–0.81) and at different waste catalyst replacement levels (0–40 wt.%). The mechanical properties of WCMBG samples, such as compressive strength and porosity, were determined after the curing process. Thermogravimetric and differential thermal analysis (TG/DTA), ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR), and scanning electron microscopy (SEM) were also used to determine their microstructural properties. When the S/L ratio was 0.76, WCMBG samples contained 10% waste catalyst exhibited greater compressive strength and lower porosity which were comparable with pure metakaolin samples. The TG/DTA results indicated that WCMBG samples contained 10 wt.% waste catalyst had more structural water and geopolymer gels. The results of ^{29}Si NMR spectroscopy of the samples showed that the major structures of the Si and Al are Q^4(3Al) and Q^4(2Al), and strong resonances were between −85 and −95 ppm, respectively. Furthermore, the waste catalyst was the compromising resource material in preparing geopolymers.

1. Introduction

The Taiwan Environmental Protection Agency reported that 11,883 tons of a waste catalyst was produced in Taiwan in 2012 [1]. The three common methods for recycling and reusing waste catalysts are landfilling, regeneration, and reuse [2]. Landfilling is not a suitable long-term solution due to the shortage of land space as well as the environmental problems caused by garbage. The DEMET process is a dominant method for reusing waste catalysts. It typically involves calcination and sulfidation (performed at approximately 1450 °F) followed by chlorination (performed at approximately 650 °F). The chlorinated product is cooled and washed, while the demetallized product is returned to the cracking unit. The filtrate is further processed in order to convert the chlorides to metal hydroxide powders. One-fifth of the total amount of the waste catalyst will be remained after this procedure, and the rest must still be disposed of. It is quite costly to invest in waste-catalyst treatment plants and only a small amount of the waste catalyst can be thus treated. Today, the reuse and recycling of waste materials after their potentialities have been detected is considered an activity that can contribute to diversify products,

---

* Corresponding author.
E-mail address: klllin@niu.edu.tw (K.-L. Lin).

http://dx.doi.org/10.1016/j.conbuildmat.2015.01.005
0950-0618/

Table 1
Chemical composition of raw materials.

Component (wt.% as oxide)	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	LOI
Waste catalyst	51.60	35.30	2.39	1.59	0.66	0.19	6.59
Kaolinite	54.90	41.80	0.712	1.59	0.01	0.22	0.46
Metakaolin	54.30	42.10	0.663	1.59	0.04	0.25	0.59

reduce production costs, provide alternative raw materials for a variety of industrial sectors, conserve non-renewable resources, save energy, and especially, improve public health [3]. Current methods for recycling and reusing a waste catalyst include employing it as an asphalt concrete filler [4], applying it in ceramic materials such as brick and floor tiles [5], and using it as a casting refractory material in China [6]. Only a few previous studies have used waste catalysts as raw materials in producing geopolymers [7]. Waste catalyst contain high levels of SiO_2 and Al_2O_3 and are often mixed with an alkaline solution to dissolve them, because SiO_2 and Al_2O_3 rapidly dissolve when waste catalyst come into contact with alkaline solutions. Therefore, waste catalyst can be used as source materials in producing waste catalyst metakaolin-based geopolymers (WCMBGs).

A new form of material with cementitious characteristics called a "geopolymer" has been developed in recent years [8]. Geopolymers are a novel type of high-performance cementitious material. Geopolymerization is a reaction that involves aluminosilicates and an alkaline solution (that acts as an activator). Any source of alumina and silica (that is readily dissolved in the alkaline solution) acts as a source of geopolymer precursor species, thereby becoming susceptible to geopolymerization. Polymerization occurs under highly alkaline conditions, when reactive aluminosilicates are rapidly dissolved and free SiO_4 and AlO_4 tetrahedral units are released into solution. Water is gradually split during the reaction, and the tetrahedral units are alternatively linked to polymeric precursors by sharing oxygen atoms between two tetrahedral units, thus leading to the formation of 3D amorphous gels in geopolymer mortars [9,10]. Compared with traditional Portland cement, geopolymers exhibit favorable properties such as more rapid compressive strength development [11], low shrinkage [12], lower permeability [13], higher resistance to acid and fire [14,15], and long-term durability [14]. In addition, geopolymers are easier to be prepared than Portland cement, requiring no high temperatures for calcining or sintering because the polymerization can be conducted at room temperature. Furthermore, geopolymer production generates nearly no NO_x, SO_x, or CO, and emits only small amounts of CO_2 [16]. These merits have contributed to a greater interest in the development of geopolymers worldwide [17].

Previous studies have concluded that the active rate of geopolymerization and the chemical composition of geopolymers depend on the fineness of the raw material, the type of aluminosilicate, and the concentration of the activator [18]. The ideal concentration of the activator increases the strength of the resulting geopolymer. The NaOH concentration in the aqueous phase of the geopolymeric system affects the dissolution process and the bonding of solid particles in the final structure [19]. Both the solid-to-liquid (S/L) and sodium silicate-to-sodium hydroxide (Na_2SiO_3/NaOH) ratios substantially affect the mechanical strength of geopolymers [20]. Xu et al. observed that activation with NaOH promoted a higher degree of dissolution of aluminosilicate solids compared with KOH [21]. This is attributed to the higher capacity of NaOH to favor the release of silicate and aluminate monomers [22,23]. Based on the provided background information, NaOH combined with a Na_2SiO_3 solution (waterglass) was used as the main activator, and the effect of different S/L ratios on the properties of WCMBG samples were observed in this study.

2. Materials and methods

2.1. Materials

The waste catalyst (51.60% SiO_2, 35.30% Al_2O_3 and 2.39% Fe_2O_3) used in this study was collected from the refinery plant located in Taoyuan City, Taiwan. Raw waste catalyst was milled using chrome steel balls and it could pass through a 0.074 mm sieve. Sodium silicate (Na_2SiO_3) solution was produced in Taiwan containing 33.81% SiO_2, 12.65% Na_2O, 53.54% H_2O, and Ms. (SiO_2/Na_2O) = 2.76. Sodium hydroxide (NaOH; 99%) was purchased from Acros. Metakaolin (specific gravities ~1.66, pH value 5.74, and the diameter size less than or equal to 0.074 mm) containing 54.3% SiO_2 and 42.1% Al_2O_3 was obtained from kaolin calcined at 650 °C for 3 h. The chemical composition of raw materials was shown in Table 1. The results showed that kaolin is mainly composed of SiO_2 (54.90%) and Al_2O_3 (41.80%). Metakaolin is composed of 54.30% SiO_2 and 42.10% Al_2O_3.

2.2. Sample preparation

The geopolymer pastes were prepared as follows: (1) an alkaline solution was made from the mixed solution of sodium hydroxide and sodium silicate in a planetary mixer for 6 min. NaOH and distilled water were mixed with a Na_2SiO_3 solution and allowed to cool to room temperature; (2) the metakaolinite and waste catalyst with the alkaline solutions was mixed in a mechanical mixer for 6 min to produce homogeneous pastes. Table 2 shows the mixing ratios of the geopolymer paste samples. The SiO_2/Na_2O ratio was 1.74 and solid-to-liquid ratio was 0.66–0.81. Waste catalyst (0%, 10%, 20%, 30% and 40%), were added into the alkali activator. The fresh paste was then rapidly poured into plastic molds (5 × 5 × 5 cm); and (3) the homogenous slurry was poured into cubic plastic molds, and the molds were sealed from the atmosphere. The samples were cured in a laboratory oven at 30 °C for 24 h before they were transferred from the molds. The compressive strength and the microstructure performance of specimens were tested after 3, 14, 28 and 56 days.

2.3. Analytical methods

2.3.1. Porosity

The porosity of the geopolymers samples was tested according to the Archimedes principle [24]. The samples were placed in a beaker of distilled water for 30 days, and then became saturated samples. The suspension weight (W_1) was mea-

Table 2
Ratios of material in mixtures.

solid/ liquid	Waste catalyst (%)	Mixture proportion by weight (g)				
		Metakaolin	Waste catalyst	Na_2SiO_3	NaOH	H_2O
0.66	0	1000	0	862.70	124.51	386.76
0.66	10	900	100	862.70	124.51	386.76
0.66	20	800	200	862.70	124.51	386.76
0.66	30	700	300	862.70	124.51	386.76
0.66	40	600	400	862.70	124.51	386.76
0.71	0	1000	0	862.70	124.51	261.81
0.71	10	900	100	862.70	124.51	261.81
0.71	20	800	200	862.70	124.51	261.81
0.71	30	700	300	862.70	124.51	261.81
0.71	40	600	400	862.70	124.51	261.81
0.76	0	1000	0	862.70	124.51	159.58
0.76	10	900	100	862.70	124.51	159.58
0.76	20	800	200	862.70	124.51	159.58
0.76	30	700	300	862.70	124.51	159.58
0.76	40	600	400	862.70	124.51	159.58
0.81	0	1000	0	862.70	124.51	74.39
0.81	10	900	100	862.70	124.51	74.39
0.81	20	800	200	862.70	124.51	74.39
0.81	30	700	300	862.7	124.51	74.39
0.81	40	600	400	862.7	124.51	74.39