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The coloring of geopolymers by the addition of copper compounds

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Abstract

The development of a new coloring technique is desirable to increase the commercial value of geopolymers. Selected copper compounds, i.e. $Cu(OH)_2$, CuO, Cu_2O, $CuCO_3$•$Cu(OH)_2$•H_2O, $CuCl_2$•$2H_2O$ and $CuSO_4$•$5H_2O$, were added to the initial reactants in order to color the geopolymers in the same manner as naturally occurring minerals. When $Cu(OH)_2$, CuO and Cu_2O were used, these compounds remained in the geopolymer matrix following hardening of the material. On the contrary, $CuCO_3$•$Cu(OH)_2$•H_2O, $CuCl_2$•$2H_2O$ and $CuSO_4$•$5H_2O$ were not detected in the final products. XAFS analyses were performed to investigate the local structure of copper in the geopolymers produced. The results showed that the copper spectra of geopolymers incorporating $Cu(OH)_2$, CuO and Cu_2O correspond to those of pure $Cu(OH)_2$, CuO and Cu_2O, respectively. However, when $CuCO_3$•$Cu(OH)_2$•H_2O, $CuCl_2$•$2H_2O$ and $CuSO_4$•$5H_2O$ were added, the copper generated spectra similar to that of the mineral chrysocolla ($(Cu, Al)_2H_2Si_2O_5(OH)_4$•$nH_2O$) than the respective copper compounds.

Keywords: C. Color; C. Mechanical properties; D. Silicate; Geopolymers; Chrysocolla

1. Introduction

Geopolymers are amorphous alkali–aluminosilicates synthesized from a combination of an aluminosilicate such as fly ash or metakaolin (produced by heating kaolinitic clay at around 700 °C) and an alkali hydroxide solution. Geopolymers are anticipated to have applications as construction materials, since their mechanical properties are similar to those of cements [1–7]. Davidovits has determined that the hardening of geopolymers occurs via the formation of a silica(IV) network accompanied by the substitution of aluminum(III) ions with alkali ions such as sodium or potassium(I) in order to maintain the charge balance of the network [1]. To date, the coloration of commercial products made of geopolymers, as a means of increasing their value, has not been studied. The addition of color to these materials would presumably be accomplishing through the addition of a pigment; however, this approach tends to produce dull colors which do not enhance the quality of the products. For this reason, we have become interested in the coloration of geopolymers using natural mineral substances which may produce better results. As an example, chrysocolla ($(Cu,Al)_2H_2Si_2O_5(OH)_4$•$nH_2O$) is an amorphous natural silicate which has a chemical composition similar to that of geopolymers and exhibits bright coloration primarily due to its copper content. Hariu et al. have reported that a chrysocolla-like structure may be obtained by conventional sol–gel techniques [8]. Therefore, the addition of copper ions derived from various copper compounds to the raw reactants can be attractive to obtain colored geopolymers.

In this study, various copper compounds were added to the initial slurry of metakaolin, sodium hydroxide solution and water glass used to make the geopolymer and the synthesis of the resulting geopolymer was monitored using FT-IR spectroscopy. The effects of the addition of the copper compound on the compressive strength of the hardened geopolymer were also investigated. X-ray absorption fine structure (XAFS) spectroscopy, which included both X-ray absorption fine structure (XANES) and X-ray absorption near-edge structure (EXAFS) analyses, was used to investigate the local structure of copper in the resulting geopolymers, and to compare these structures to those found in the naturally-occurring mineral chrysocolla.

2. Experimental procedure

The raw materials used were metakaolin (Tomoe Kougyou Co., Ltd., Japan), potassium water glass (SiO_2: 27.5–29%;

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K_2O: 21–23%; Fuji Kagaku Co., Ltd., Japan), potassium hydroxide (99%; Kishida Chemical Industries, Ltd., Japan) and distilled water. The copper compounds employed in this work were $Cu(OH)_2$ (90%), CuO (99%), Cu_2O (90%), $CuCO_3$•$Cu(OH)_2$•H_2O (98%), $CuCl_2$•$2H_2O$ (99%) and $CuSO_4$•$5H_2O$ (99.5%), all sourced from Kishida Chemical Industries. The chemical composition of the metakaolin is presented in Table 1. The starting materials used for the synthesis of the geopolymers are shown in Table 2. In all the samples, the Cu/metakaolin mass ratio was maintained at approximately 2.5%. Test specimens were fabricated from slurry mixtures composed of metakaolin, potassium silicate solution, potassium hydroxide and distilled water. The materials made using $Cu(OH)_2$, CuO, Cu_2O, $CuCO_3$•$Cu(OH)_2$•H_2O, $CuCl_2$•$2H_2O$ and $CuSO_4$•$5H_2O$ are denoted as B–OH, B–O, B–2O, B–CO, B–Cl and B–SO, respectively. The same amount of water was added for the preparation of the samples with the exception of sample B–Cl, which required more water for casting the slurry. Each slurry mixture was cast into a cylindrical acrylic mold (∅15 mm × 30 mm high), one end of which was capped, and cured at 80 °C and 50% relative humidity for 72 h inside a temperature and humidity controlled (THC) chamber.

The crystalline phases of the resulting bulk products were determined by powder X-ray diffraction analysis (XRD: XD-D1; Shimazu Co., Ltd., Japan) and the compressive strengths of the samples were measured using an Instron 5582 (Instron Co., Ltd., USA) at a crosshead speed of 10 mm/min. Three to five test pieces were prepared and tested for each different additive. In order to confirm the formation of a geopolymer, FT-IR spectra of the samples were acquired using the KBr pellet method with a Spectrum 100 instrument (PerkinElmer Inc., USA). Cu K-edge X-ray absorption profiles were obtained via XAFS analysis using the BL5S1 beamline of the Aichi Synchrotron Radiation Center (Aichi Science and Technology Foundation, Japan). A sample of the naturally-occurring blue-green mineral chrysocolla (Kalukuluku, Shaba Prov., Congo) was used as a reference material. All X-ray absorption measurements were carried out in transmission mode at room temperature.

Table 1
Chemical composition of the metakaolin employed in this work.

Composition	Mass%
SiO_2	52.7
Al_2O_3	44.8
Na_2O	0.4
K_2O	0.1
CaO	0.2
P_2O_5	0.6
Fe_2O	0.3
TiO_2	0.7
MgO	0.1
Total	99.9

3. Results and discussion

3.1. Properties

Fig. 1 shows a photographic image of the resulting colored bulk materials with and without the addition of copper compounds. Without a copper compound, the geopolymer sample is beige in color. In contrast, the B–2O and B–O materials are dark pink and gray, respectively, while the B–OH, B–Cl, B–SO and B–CO are pale blue-green.

Fig. 2 plots the compressive strength of the bulk materials. It is evident that, with the exception of the B–Cl sample, adding a copper compound has minimal effect on the strength. The B–Cl is the only material which shows a low value of compressive strength, which is attributed to its higher water content as shown in Table 2, since increasing water content generally leads to a decrease in the compressive strength of the hardened material [3]. According to Fig. 2, the addition of a copper compound into the starting raw materials for the purposes of adding color does not negatively affect the

Fig. 1. Photograph of the resulting bulk samples with and without copper compounds.

Table 2
Composition of the starting materials used to produce geopolymers.

Sample name	Metakaolin	K-water glass	KOH	H_2O	$CuCl_2\cdot 2H_2O$	$CuCO_3\cdot Cu(OH)_2\cdot H_2O$	$CuSO_4\cdot 5H_2O$	$Cu(OH)_2$	CuO	Cu_2O
B–CO	100	40	10	20	–	5	–	–	–	–
B–Cl	100	40	10	40	7.5	–	–	–	–	–
B–SO	100	40	10	20	–	–	10	–	–	–
B–OH	100	40	10	20	–	–	–	4	–	–
B–O	100	40	10	20	–	–	–	–	3.5	–
B–2O	100	40	10	20	–	–	–	–	–	3