



# Novel coloring of geopolymer products using a copper solution immersion method



Shinobu Hashimoto\*, Hayami Takeda, Sawao Honda, Yuji Iwamoto

Nagoya Institute of Technology, Department of Environmental and Materials Engineering, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

## HIGHLIGHTS

- Novel coloring of geopolymer products by immersion into a copper chloride solution has been performed.
- It was clarified that there were two coloring processes in green.
- One was the precipitation of atacamite crystals.
- The other was the diffusion of copper ions into geopolymer products.

## ARTICLE INFO

### Article history:

Received 3 September 2014  
Received in revised form 9 March 2015  
Accepted 10 April 2015  
Available online 29 April 2015

### Keywords:

Coloring  
Geopolymers  
Geopolymer products  
Copper ion  
Atacamite  
Solution immersion method

## ABSTRACT

Geopolymer products were fabricated from a slurry composed of metakaoline, potassium silicate solution, and potassium hydroxide with a mass ratio of 57.1:34.3:8.6, which was cured at 60 °C and 100% relative humidity for 1 week. The hardened geopolymer products were immersed in a 0.1 mol/L copper chloride solution at 25 °C for 1–168 h. The copper chloride solution to geopolymer product mass ratio was maintained at 2.5. According to visual observations, the spread of color from the surface to the interior of the geopolymer product seemed to stop once the immersion time reached 24 h. After immersion for 168 h, atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) crystals were partially formed on the geopolymer product surface and at depths of 150–300  $\mu\text{m}$ . These precipitated atacamite crystals contributed to a green coloration of the sample. However, the observed green coloration, which reached a depth of approximately 900  $\mu\text{m}$  in the geopolymer product after an immersion time of 168 h, was mostly caused by the presence of isolated copper ions due to the substitution of potassium ions in the geopolymer product by copper ions from the solution. Thus, two coloring mechanisms were active in this system.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Generally, geopolymer cements or Portland cements made from fly ash have a gray or gray-like color. A simple method of coloring these cements should significantly increase the value of the resulting manufactured cement products. Generally, inorganic pigments are added to the raw materials of the concretes or other cement based products [1–4]. In this coloring process, the added pigments do not remain in the hardened cement bodies; that is, the pigments remain within the hardened concrete or other cement based product bodies. According to some cost assessment, novel coloring methods for concrete and cement products will be expected to develop.

It has been reported that geopolymers consist of a silica network, with aluminum ions attracted by univalent alkali ions due to the charge valance [5]. In this network structure, silicon ions can be substituted by other transition elements with an ionic diameter similar to that of the silicon ion. For example, a copper ion could exchange with a silicon ion in the silica network structure of the geopolymer. Among natural gemstones, chrysocolla ( $\text{Cu}, \text{Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ) is an amorphous phase which is thought to be similar to the geopolymer structure with copper [6]. Therefore, we recently attempted to fabricate geopolymers with a chrysocolla-like green color by adding copper-based salts to the starting materials. When copper carbonate, copper sulfate, and copper chloride were used, these original copper salts were not detected in the geopolymers after hardening. This suggests that a chrysocolla-like structure was formed inside the geopolymers.

Because geopolymers contain micropores due to their zeolite semistructure [7], even though they have an amorphous overall

\* Corresponding author.

E-mail address: [hashimoto.shinobu@nitech.ac.jp](mailto:hashimoto.shinobu@nitech.ac.jp) (S. Hashimoto).

structure, geopolymers may be applicable in materials designed for the absorption of water vapor, organic odors, or ions in solution [8]. Therefore, it was thought that potassium ion exchange treatment of a geopolymer with transition element ions in certain solutions could generate unique colors in the geopolymer products. However, the coloration of a geopolymer product by immersion in a transition element ion solution has not yet been reported. Here, if a copper chloride solution is used as a transition element ion solution, there is a possibility that atacamite crystals will be also precipitated and show a unique green color, except copper ion exchange effect [9,10]. Atacamite crystals are stable in atmosphere and so far they have been detected as a natural pigment in the copper patina compounds of historical sculptures [11–14]. Hence, immersion in a copper chloride solution for the coloration of geopolymer products is thought to be convenient, unique and low cost method.

In this study, geopolymer products fabricated from metakaoline were immersed in a copper chloride solution to provide a green coloration to the geopolymer products. After immersion treatment for various lengths of time, precipitated copper compound crystals at the surface and/or interior of the geopolymer product were analyzed by X-ray diffraction (XRD), and their morphology was observed using scanning electron microscopy (SEM). The diffused copper ions that did not crystallize within the geopolymers were also analyzed using energy dispersive spectroscopy (EDS), and the chemical state of the copper ions in the geopolymer product was analyzed by electron spin resonance (ESR). Furthermore, in order to investigate the formation mechanism of the copper compound crystals, the geopolymer products were immersed in pure water or copper chloride solution, and the changes in pH over time were monitored. Finally, the mechanism of geopolymer product coloration in this copper chloride solution immersion method was clarified.

## 2. Experimental procedure

Commercial metakaoline, with the chemical composition shown in Table 1, was used as a starting material. A mixed slurry composed of metakaoline, potassium silicate solution (water glass; 18.9–19.4 mass%  $\text{SiO}_2$ , 8.5–9.0%  $\text{K}_2\text{O}$ ), and 85 mass% potassium hydroxide solution with a composition ratio of 57.1:34.3:8.6 (mass%), was added to a cylindrical acrylic tube 16 mm in diameter with one side closed. The sample cylinders were placed in a temperature and humidity controlled chamber, which was kept at 60 °C and 100% relative humidity for 1 week to form hardened bodies. Regent grade  $\text{CuCl}_2(\text{H}_2\text{O})$  was dissolved in fresh water to form a 0.1 mol/L copper chloride solution. Subsequently, the resultant geopolymer products were immersed in a copper chloride solution at 25 °C for 1–168 h. The mass ratio of copper chloride solution to geopolymer product was kept at 2.5. After this immersion treatment, the samples were dried at 40 °C for 48 h without humidity control. The newly formed crystal phases of the colored samples were analyzed by X-ray diffraction (XRD: X'Pert-MPD; PHILIPS), and the morphology of the crystal phases was observed by scanning electron microscopy (SEM: JSM-6010LA; JEOL). In the XRD analysis, each fixed region of the geopolymer product which was removed using a polishing paper with 9  $\mu\text{m}$  alumina particles from its surface was directly analyzed step by step. For the observation of micromorphology, gold sputtered coat was performed on the sample and the accelerating voltage of electric beam was

**Table 1**  
Chemical composition of the metakaoline used.

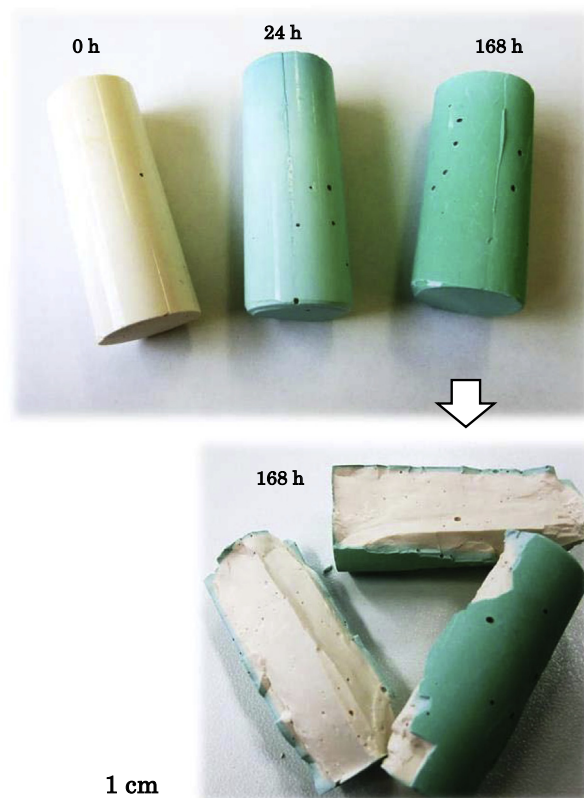
Composition/mass%	
$\text{SiO}_2$	53.20
$\text{Al}_2\text{O}_3$	43.30
$\text{Na}_2\text{O}$	0.01
$\text{K}_2\text{O}$	1.06
$\text{MgO}$	0.01
$\text{P}_2\text{O}_5$	0.61
$\text{CaO}$	0.01
$\text{TiO}_2$	0.40
$\text{Fe}_2\text{O}_3$	1.10
Total	99.70

10 kV. Furthermore, the distributions of copper and chlorine ions inside the geopolymer product were analyzed using energy dispersive spectroscopy (EDS) equipment installed on the above SEM. With elemental analysis, the integration time for taking an image and accelerating voltage of electric beam were 10 min and 15 kV, respectively. Changes in the concentration of the copper chloride solution after the immersion test were determined by inductively coupled plasma (ICP; ICPS-7000; SHIMADZU) analysis. Based on the calibration curve prepared from copper ion standard solutions, the actual concentrations of the copper chloride solutions were calculated from the measured values. In order to clarify the state of the copper atoms in the geopolymer product, electron spin resonance (ESR: JFS-FA200; JEOL) was performed for the green colored region of the geopolymer product which was removed using a diamond wheel and ground to a powder. The output power was 1.00 mW. When lone paired electrons are in the static magnetic field, absorbance of microwave with a specific frequency occurs. Therefore, if there are isolated copper ions, the corresponding spectrum will be obtained. Finally, changes in the pH of water and copper chloride solutions with geopolymer product immersion time were monitored by a pH meter (D-51; HORIBA).

## 3. Results and discussion

### 3.1. Formation of atacamite crystals

Fig. 1 shows the appearance of geopolymer products after immersion treatment for various durations. This figure also shows a cross-section of a sample after immersion treatment for 168 h. As shown in the figure, green coloration was observed not only at the surface, but also within the geopolymer product, up to a depth of 1 mm. Fig. 2 shows optical photographs of geopolymer product cross-sections after 3, 24, and 168 h of immersion treatment. After reaching a depth of approximately 870  $\mu\text{m}$  after 24 h of immersion, the green color did not spread much deeper into the sample. That is, the depth of green coloration after 168 h of immersion was only 920  $\mu\text{m}$ , which was not significantly deeper than after 24 h of immersion. However, according to ICP analysis of the remaining copper chloride solution, the concentrations of the



**Fig. 1.** Optical photographs of geopolymer products after immersion times of 0, 24, and 168 h, and a cross-section of a 168 h immersed geopolymer.

Download English Version:

<https://daneshyari.com/en/article/256960>

Download Persian Version:

<https://daneshyari.com/article/256960>

[Daneshyari.com](https://daneshyari.com)