



Detoxification and solidification of heavy metal of chromium using fly ash-based geopolymer with chemical agents



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HIGHLIGHTS

- Different dosages and chemical valences of chromium obviously affect geopolymers.
- Chromium affects compressive strength, reaction products and pore structures of geopolymers.
- Chemical bonding and physical encapsulation coexisting in chromium containing geopolymers.
- DTCR has a good detoxification performance in chromium containing geopolymers.

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ABSTRACT

Geopolymers are new cementitious materials that with 3 dimensional networks, which can effectively solidify/stabilize heavy metals. Utilization of fly ash as precursor to prepare geopolymers, and influences of dosages and chemical valences of chromium reagents on geopolymers, as well as detoxification effectiveness of chemical agents for geopolymers were studied. The results showed that compressive strength of geopolymers could be improved when dosage of $\text{Cr}(\text{NO}_3)_3$ is small. Reinhardbraunsite ($\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$) was generated in geopolymers with $\text{Cr}(\text{NO}_3)_3$ or CrO_3 due to 'ions exchange'. Respectively dosing Cr_2O_3 , Cr and CrO_3 could make total pore volume of geopolymers smaller and make geopolymers more compact. Chemical bonding and physical encapsulation both existed in geopolymers. Chemical bonding played main role in geopolymers with $\text{Cr}(\text{NO}_3)_3$, and physical encapsulation played main role in geopolymers with Cr_2O_3 , Cr and CrO_3 , respectively. Chemical agent DTCR could effectively improve compressive strength and capture Cr^{3+} of geopolymers, enhancing their abilities of anti-erosion.

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1. Introduction

With the accelerated process of industrialization, a variety of solid wastes contained heavy metals are produced, especially a lot of chromium compounds are produced in the process of iron and steel smelting and electroplating process. They have various chemical valences and complex binding modes, they are not only hard to be decomposed by microorganism, but also easy to chemically generate in organisms and become more toxic compounds, which have been a threaten to the health and living environment of human.

Traditional cementitious materials were recognized as solidify materials in early stage, but the shortages of cement solidified bodies are high permeability and heavy metals leaching concentration,

as well as poor durability [1]. J. Davidovits et al. believed that cement and other traditional inorganic cementitious materials were not suitable to deal with solid wastes contained heavy metals [2,3]. Geopolymers are new generation of aluminosilicate inorganic cementitious materials. They are generally synthesized by activation of an aluminosilicate source (natural mineral, artificial silicon aluminum compound and solid wastes) with an alkaline hydroxide or silicate solution [4,5]. Due to the "Cage" structure of the geopolymer gel like zeolite, they have great advantages in solidifying/stabilizing heavy metals.

Fly ash is an industrial wastes generated from the coal-fired power station, metallurgical industry, and chemical industry. Especially using coal to generate electricity that produce a large number of fly ash, accounting 15–40% weight of the raw coal. Recently, annual production of fly ash in the world is about 800 million ton, and dramatically increases due to the large demand of power in China and India since 2004 [6]. Fly ash is rich SiO_2 and Al_2O_3 which is potential to be prepared as geopolymers.

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Chemical agents can make toxic and harmful components to be low solubility, low mobility, and low toxic substance through chemical reaction. According to the types of heavy metals which contained in wastes, chemical agents can be divided into inorganic chemical agents and organic chemical agents. Inorganic chemical agents are including gypsum, bleaching powder, phosphate, sulfide, etc. [7–10]. Organic chemical agents are including dithiocarbamates (DTCR or DTC), ethylenediaminetetraacetic acid (EDTA), etc. [11–13]. They have good effects in the treatment of heavy metals.

This work planned to use fly ash-based geopolymer to solidify/stabilize heavy metals, and chemical agents were used as supplementary. The effects of chromium on the compressive strength, reaction products, and pore structures of fly ash-based geopolymer were studied. The mechanism of solidification/stabilization of chromium by geopolymers was explored. The detoxification effectiveness of chemical agents for geopolymers that with heavy metals was researched. This work helps to open up a new approach for reusing solid wastes contained chromium, and give reference to broaden the application and security guarantee of the waste-based geopolymers.

2. Experimental procedure

2.1. Materials

Fly ash used in this experiment is from a company in Shanghai, whose specific surface area is about 370 m²/kg. Chemical components are listed in Table 1 and XRD pattern is shown in Fig. 1. The main phases of this fly ash are Quarts, Mullite, Calcium Oxide, and Corundum.

The solid mass ratio of sodium silicate is 42.7% (13.2% Na₂O and 29.6% SiO₂, initial modulus is 2.32). NaOH is from the Chinese Medicine Group Chemical Reagent Co., Ltd., purity is 96.0%. NaOH was used to adjust sodium silicate to obtain composite chemical activator whose modulus ($M = n(\text{SiO}_2)/n(\text{Na}_2\text{O})$) is 1.5.

Four types of chromium reagents, Cr(NO₃)₃, Cr₂O₃, Cr and CrO₃, are also from the Chinese Medicine Group Chemical Reagent Co., Ltd., The purities of all the chromium reagents are 99.0%.

In this experiment, four kinds of detoxification agents, i.e., chemical agents of Na₂S, NaH₂PO₄, (2, 4, 6-trithione-1, 3, 5-triazine trisodium salt, TMT), and dithiocarbamate (DTCR) were used to improve the solidifying/stabilizing effectiveness of the fly ash-based geopolymer with heavy metals. The purities of Na₂S and NaH₂PO₄ are 98.0% and 99.0%, respectively. The solid mass ratios of TMT and DTCR are 15.0% and 40.0%, respectively.

2.2. Geopolymers synthesis

By referring to the preparation technology of cement paste, geopolymers were prepared according to mix proportion. They were slowly stirred for 120 s, then stopped for 15 s, at last quickly stirred for 120 s. The pastes were put into mould with the size of 20 mm × 20 mm × 20 mm, and were vibrated to remove bubbles, then were slicked. They were cured for 24 h in the temperature of 20 ± 1 °C and relative humidity of 95% ± 1%, then removed the mould. At last, they were cured for design ages which are sealed with plastic film.

In this experiment, four different dosages (0, 0.5%, 1.0% and 1.5%) of Cr(NO₃)₃, were chosen, and the effects of dosage of Cr(NO₃)₃ on geopolymers were studied, including compressive strength, reaction products, and pore structures on geopolymers curing for 28 days. The mix proportions of geopolymers samples that with different dosages of Cr(NO₃)₃ are listed in Table 2.

Four types of chromium reagents (Cr(NO₃)₃, Cr₂O₃, Cr and CrO₃) were mixed in fly ash-based geopolymers. Compared with the blank geopolymer sample F, the effects of different chemical valences of chromium reagents on fly ash-based geopolymer samples curing for 28 days, including compressive strength, reaction products and pore structures were studied. The mechanism of solidification/stabilization of chromium reagents by geopolymers were analyzed. The mix proportions of geopolymers that with different chemical valences of chromium reagents are listed in Table 3.

Table 1
Chemical compositions of fly ash.

Chemical compositions	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Fe ₂ O ₃	K ₂ O	CaO	TiO ₂	Loss
Content/%	0.45	0.85	22.40	40.70	0.71	2.17	5.34	0.69	9.46	1.16	16.09

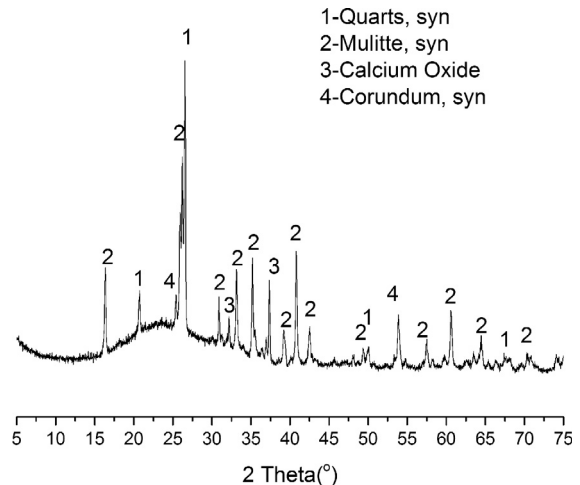


Fig. 1. XRD pattern of fly ash.

In order to improve the solidifying/stabilizing effectiveness of these solidified geopolymer bodies with Cr(NO₃)₃, four chemical detoxification agents (Na₂S, NaH₂PO₄, TMT and DTCR) were chosen and dosed in fly ash-based geopolymers. In the solidified geopolymer samples, these four chemical detoxification agents simply marked as S, P, T, D, respectively. These solidified bodies with chemical detoxification agents were compared to the blank sample F-Cr(NO₃)₃. The detoxification of chemical agents has been analyzed through compressive strength, leaching toxicity, as well as microstructures that before leaching and after leaching for 14 days. The mix proportions of these solidified geopolymer bodies with different chemical detoxification agents are listed in Table 4.

2.3. X-ray diffraction spectrometer (XRD)

The minerals composition of the geopolymer samples curing for 28 days (Samples in Tables 2 and 3) were tested by XRD. A Siemens-Bruker D5000 powder diffractometer with Cu-K α radiation in the theta/ θ configuration was used for measurements. The diffractometer was operated at 40 kV and 30 mA. Measurements were made from 5° to 75° 2 θ at a rate of 1°/min with a step size of 0.02° (2 θ).

2.4. Brunauer-Emmett-Teller (BET)

The specific surface area of 28 days geopolymer samples in Tables 2 and 3 were tested by BET. Specific surface area test range of 3H-2000PS1/2 BET is above 0.01 m²/g, and aperture measurement range is tested from 0.35 nm to 200 nm.

2.5. X-ray photoelectron spectroscopy (XPS)

Geopolymer samples in Table 3 curing for 28 days were tested by XPS. Through XPS, change of binding energy of O1s, Si2p and Al2p will be obtained. Vacuum degree of ESCALAB 250Xi XPS is 4.3 × 10⁻¹⁰ mbar, energy resolution is 0.44 eV, and sensitivity is 3.28 Mcps.

2.6. Environmental scanning electron microscope (ESEM)

Geopolymer samples in Table 3 curing for 28 days, as well as the system of F-Cr(NO₃)₃-1.0 with chemical detoxification agents before leaching and after leaching for 14 days were tested by ESEM. Acceleration voltage of Quanta 200 ESEM is 500V–30 kV. Resolution ratios both in high vacuum mode and environmental scanning mode are <2 nm. Energy spectrum resolution is 132 eV.

2.7. Inductively coupled plasma-atomic emitted spectrometer (ICP-AES)

Leaching tests of geopolymer samples in Table 4 curing for 28 days were conducted according to the "Solid Waste-Extraction Procedure for Leaching Toxicity-Horizontal Vibration Method" (HJ 557-2010). ICP-AES was used to obtain concen-

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