

## Detoxification/immobilization of hexavalent chromium using metakaolin-based geopolymer coupled with ferrous chloride

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### ABSTRACT

The detoxification and immobilization of Cr(VI) using metakaolin-based geopolymer coupled with ferrous chloride was solved successfully. Adding potassium dichromate and ferrous chloride in the base colloid formed by mixing metakaolin and the alkaline activator, Cr(VI)-contaminated metakaolin-based geopolymer was prepared, whose compressive strength was more than 30 MPa. The optimized capacity of chromium in the geopolymer was 0.8 wt.% with an optimized Fe<sup>2+</sup>/Cr(VI) mole ratio of 4:1, which ensured a low leached chromium concentration below 5 mg/L. This product was mainly amorphous except by-product sodium chloride. According to XRD, SEM and XPS, the mechanism of Cr detoxification/immobilization was speculated and explained. In the colloid, the negatively charged [AlO<sub>4</sub>] was first formed because of the geopolymerization, and at the same time, Cr(VI) was reduced to Cr<sup>3+</sup> under the participation of Fe<sup>2+</sup>. Then, Cr<sup>3+</sup> was attracted by [AlO<sub>4</sub>] due to the electrostatic attraction and stabilized in geopolymer matrices. Therefore, the immobilization of Cr(VI) in geopolymer contained a redox and a fixation process. This method is expected to be used for the disposal of Cr(VI)-contaminated solid wastes.

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### 1. Introduction

Geopolymer, typically synthesized from aluminum silicate mineral or solid waste by activation of alkaline, represented a kind of amorphous inorganic polymer composed by [SiO<sub>4</sub>] and [AlO<sub>4</sub>] tetrahedrons [1]. Because of the raw material's selection and reaction conditions, geopolymers can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, acid resistance, fire resistance, high durability under natural conditions and low permeability [1–3], resulting in a variety of potential applications [4–10]. Because of [AlO<sub>4</sub>] tetrahedron with negative charge in geopolymer, more attraction had been focused on the immobilization of metal cations by charge neutralization in recent years, such as Zn<sup>2+</sup>, Co<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Sr<sup>2+</sup>, Cd<sup>2+</sup> and Cs<sup>+</sup> [11–19]. However, for the highly toxic Cr(VI) which existed as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anion [20,21], geopolymer failed in Cr(VI) immobilization, leading to the free diffusion of the water-soluble Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> from geopolymer matrices. But sodium sulfide

(Na<sub>2</sub>S) introduced in fly ash based geopolymer reduced dramatically the concentration of Cr(VI) in the leachate [22]. The method of adding the ferrous sulphate heptahydrate in Portland cement to remove soluble Cr(VI) was ever reported [23]. Obviously, if Cr(VI) was immobilized successfully in geopolymer or Portland cement, it must be converted to chromium cation form firstly, such as Cr<sup>3+</sup>, which can be fixed in the matrices as other heavy metal cations. This is a very effective method to remove the toxicity of Cr(VI). So, it motivates us to further envision the adaptability and feasibility of using the geopolymer coupled with other reductants, such as FeSO<sub>4</sub>, FeCl<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub>, for the disposal of Cr(VI) and explore the immobilization capacity of cations.

This present work mainly shed light on the disposal of Cr(VI) by using metakaolin-based geopolymer coupled with FeCl<sub>2</sub>·4H<sub>2</sub>O. The detoxification/immobilization of Cr(VI) was studied by simulation experiments. It is concerned about the immobilization capacity of chromium, mineralogy and mechanical property of the geopolymer matrices added with FeCl<sub>2</sub>·4H<sub>2</sub>O, and the explanation of chromium immobilization mechanism in the meta-kaolinite-based geopolymer.

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## 2. Experimental

### 2.1. Materials

Kaolin used in the experiments was from Datong, Shanxi province, PRC, with 86% of particle size below 2  $\mu\text{m}$ . The kaolin was dried at 105  $^{\circ}\text{C}$ , crushed for 2 min and then calcined at 600  $^{\circ}\text{C}$  for 4 h to harvest metakaolin product (denoted by MK) with high pozzolanic activity, which was used as raw material in geopolymerization. The chemical composition of kaolin measured by XRF is listed in Table 1.

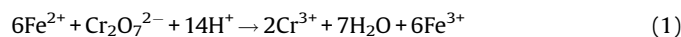
The sodium silicate (modulus 2.8, Baume degrees 45, Foshan Zhongfa sodium silicate factory, China) and other chemical-grade reagents, including NaOH,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  (Sinopharm Chemical Reagent Co., Ltd., China) were used as received. The deionized water was used in all experiments.

### 2.2. Geopolymerization

The alkaline activator solution was obtained by dissolving NaOH in the sodium silicate solution. Then MK was added into the above solution and stirred for 20 min until the homogeneous colloid was formed, where the mass ratio of MK, sodium silicate solution and NaOH were set to be 6:5:1. The colloid was then casted into the stainless steel cubic mold (20 mm  $\times$  20 mm  $\times$  20 mm) and vibrated for 2 min to eliminate air bubbles. The sample in the mold was next put in an oven at 90  $^{\circ}\text{C}$  with 100% humidity for 30 min to accelerate hardening. After that, the cubic-shaped sample was demolded and sealed in the polyethylene (PE) film and then cured in water bath at 60  $^{\circ}\text{C}$  for 2 h. Finally, the pure metakaolin-based geopolymer was obtained and denoted as MG.

To study the detoxification and immobilization of Cr(VI) in MG, the saturated solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  were successively added during preparation of MG colloid and the other procedures remained unchanged.

In theory, the reaction of  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  occurs in acidic condition according to the following equation:



The theoretical molar ratio of  $\text{Fe}^{2+}/\text{Cr(VI)}$  is 3:1 and the mass ratio of  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}/\text{K}_2\text{Cr}_2\text{O}_7$  is about 6:1. However, the reaction in our experiments underwent under alkaline conditions.  $\text{Fe}^{2+}$  would partially be consumed by hydroxyl to produce  $\text{Fe(OH)}_2$  in the colloid, which may cut off the geopolymer network. So, saturated solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  should be added firstly and saturated solutions of  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  later added in MG colloid in order to reduce the contact time of  $\text{Fe}^{2+}$  and  $\text{OH}^-$ . The addition of Cr(VI) was set to 0.1 wt.% of the mass of pure MG, correspondingly the addition of  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  within a range of 1–3.0 wt.% of the pure MG colloid. The samples prepared were denoted as MGF. The optimal ratio of  $\text{Fe}^{2+}/\text{Cr(VI)}$  would be figured out according to the leached Cr concentration of as-synthesized samples without destroying the integrity network of geopolymer. After that, the addition amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  would be increased by proportion in the pure MG colloid to determine the maximal capacity of Cr fixed in the geopolymer, and the relevant samples were represented by MGF<sub>C</sub>.

Before the tests were performed, all the samples were sealed by the PE film and cured at room temperature for one day.

### 2.3. Test methods

#### 2.3.1. Leachate testing

The toxicity characteristic leaching procedure (TCLP) test was conducted according to US EPA Method 1311 [24]. The samples were pulverized to fragments with the largest sizes below 9.5 mm. The extraction liquid, with a pH value of 2.88, was prepared by dissolving 5.7 mL of glacial acetic acid in 1 L of deionized water. A certain amount of extraction liquid was added to a PE container with the geopolymer fragments, with a liquid to solid ratio (L/S) of 20:1, followed by a rolling-over process at 30 rpm for 20 h on an oscillator. The leachate from the samples was filtrated by a polycarbonate filter with an effective pore size of 0.45  $\mu\text{m}$ . Chromium concentrations were determined by flame atomic absorption spectrophotometer with a WFX-110 spectrometer and inductively coupled plasma mass spectrometry (ICP-MS, Elan DRC-e, PerkinElmer).

#### 2.3.2. Property characterization

The chemical composition of metakaolin was determined by the X-ray fluorescence (XRF, AXIOSmAX, PANalytical B.V.). The compressive strength of samples was measured according to the Chinese Standard (GB/T 17671-1999) on a WE-50 universal testing machine (Shandong Jinan Testing Machine Factory, China), by averaging from three bricks for each composition. The mineral phases of the samples were determined by the X-ray powder diffraction (XRD, D8-FOCUS, Bruker AXS), with step-scanning in the  $2\theta$  range from 5 to 70 $^{\circ}$  at a rate of 4 $^{\circ}$ /min using Cu K $\alpha$  radiation and Ni filter at a generator voltage of 40 kV and a current of 40 mA. The micromorphology of the sample surface and the main elements distribution were characterized by using a field emission scanning electron microscope (FESEM, SU8010, Japan) with an accelerating voltage of 5 kV. The binding energies of Cr2p and Fe2p in geopolymer specimens were determined by the X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, Thermo) with 12.5 kV voltage, 20 mA current, X-ray source of Al K $\alpha$ , energy step size of 0.05 eV, taking C<sub>1s</sub>284.6 eV as the energy calibration standard.

## 3. Results and discussion

### 3.1. Leached chromium concentrations

The leached chromium concentration from all samples is shown in Fig. 1. When the  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  addition increased from 0.5 wt.% to 1.5 wt.% in MG colloid with a constant addition (0.1 wt.%) of Cr(VI), the leached chromium concentration from MGF samples decreased dramatically, from 20.05 mg/L to 0.42 mg/L (Fig. 1A). After that, when the  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  addition went on increasing from 1.5 wt.% to 3.0 wt.%, the curve of the leached chromium concentration fluctuated slightly, from 0.42 mg/L to 0.135 mg/L, which was far below 5 mg/L, the upper limit of chromium leaching rate from nonhazardous wastes stipulated by the US EPA standard. Therefore, for an addition amount of 0.1 wt.% Cr(VI), the  $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$  addition must be equal or more than 1.5 wt.%, corresponding to  $\text{Fe}^{2+}$

**Table 1**  
Chemical composition of metakaolin measured by the X-ray fluorescence (XRF).

Chemical composition	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	CaO	MgO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{P}_2\text{O}_5$	LOI <sup>a</sup>
Content (wt.%)	52.01	42.75	0.42	0.34	0.18	0.08	0.29	0.41	0.44	3.08

<sup>a</sup> LOI: Loss on ignition at 1000  $^{\circ}\text{C}$

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