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Formulation and durability of a geopolymer based on metakaolin/tannery sludge

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ABSTRACT

In this study, tannery sludge was used as a partial replacement material for a geopolymer. The best raw material composition of the geopolymer and durability of the solidified product were studied. Solidification effect was analyzed via compressive strength and total concentration of chromium leached. Its durability in terms of high-temperature resistance, acid/base resistance property, and resistance to acid rain erosion was studied. Through X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric Differential Thermal Analysis (TG-DTA) and scanning electron microscopy (SEM), the compressive strength and total concentration of chromium leached in different environments were analyzed. The results show that the mechanical properties of the solidified product were optimal when the silica/alumina mole ratio and sodium oxide/silica mole ratio were 2.45 and 0.37, respectively. The optimal raw material ratio of the above-mentioned product was used to synthesize a geopolymer containing 20% tannery sludge, with the solidified product showing high durability, as indicated by its good high-temperature resistance, high resistance to acids and alkalis, and great resistance to acid rain erosion.

1. Introduction

Tannery sludge is commonly considered to be hazardous waste because of its high chromium ions content. There are two main sources of leather sludge: (1) chromium-rich sludge, which is separated from the chromium tanning wastewater during deposition with lime and flocculants (Kavouras et al., 2015); (2) waste activated sludge, which is formed via biochemical treatment (Alibardi and Cossu, 2016). The disposal of tannery sludge is a major problem in the leather industry. Different methods for tannery sludge management have been reported, such as sludge incineration and landfilling. Although incineration is widely used (Alibardi and Cossu, 2016; Zupancic and Jemec, 2010), it has certain limitations. The transformation of trivalent chromium to hexavalent chromium occurs at high temperatures. Landfilling is a suitable approach only if the heavy-metal discharge is below an acceptable level; hence, heavy metals should be removed or stabilized (Cossu, 2010). In addition, resources are utilized in agriculture. The principal topic of this study is the fate of heavy metals and their effects on plant and soil quality (Patel and Patra, 2014; Vig et al., 2011). Recently, bioleaching has been reported as a cost-effective way for recycling trivalent chromium in tannery sludge. Bioleaching focuses on improving the quality of tannery sludge for sustainable disposal (Ma et al., 2017).

Solidification methods are an effective way of treating hazardous waste (Shi and Fernandez-Jimenez, 2006). However, ordinary Portland cement presents many shortcomings when used with hazardous waste, such as poor corrosion resistance, low durability, high heavy-metal leaching rate, and high enlargement ratio. Recently, a geopolymers have been used as an alternative material for treating hazardous wastes. Geopolymers are novel inorganic polymers with a cage-like zeolite structure. Their basic structures are the SiO_4 tetrahedron and AlO_4 tetrahedron (Davidovits, 1991). They are the reaction product of solid aluminum silicate salt and high concentrations of alkali and silicate and are amorphous or semicrystalline materials (Guo et al., 2017). Because of their high compressive strength and low permeability, geopolymers are believed to be a curing system that can solidify various hazardous wastes (Jin et al., 2016). In contrast to the production of ordinary Portland cement, the synthesis of a geopolymer requires low energy and generates fewer carbon dioxide emissions (McLellan et al., 2011). The reported prospective studies on the stabilization of heavy metals using geopolymers are numerous (El-Eswed et al., 2017; El-Eswed et al., 2015). Some scholars have focused on the development of raw materials especially for industrial

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wastes such as bottom ash (Boca Santa et al., 2016) and municipal solid waste incineration fly ash (Jin et al., 2016). Material modification is also a relevant research direction. For example, straw has been used as an additive for improving thermal insulation properties (Toguyeni et al., 2012). In addition, many other additives have been used in various studies, such as fiber material, nano-SiO_2, and nano-Al_2O_3.

Tannery sludge contains many pollutants, and thus is harmful without suitable treatment. In this study, a geopolymer was used for the disposal of tannery sludge. We solidified tannery sludge with a geopolymer and studied its physical properties and durability under harsh conditions to explore whether addition of tannery sludge changes the geopolymer structure.

2. Materials and methods

2.1. Materials

2.1.1. Kaolin and metakaolin

The metakaolin used was obtained by calcining pure kaolin (industrial grade; Suzhou, China) at 800 °C for 2 h. The main chemical components of metakaolin (Table 1) were analyzed on an X-ray fluorescence (XRF) spectrometer (ARL Advant'X, Thermo, USA).

The XRD results for the metakaolin are shown in Fig. 1. It can be seen from the figure that the main phase of metakaolin is SiO_2, with a small amount of $Al_2Si_2O_5(OH)_4$ and TiO_2.

It can be seen from the XRD pattern that the main component of metakaolin is amorphous phase aluminosilicate. Amorphous phase is highly active and can be easily activated by alkali activators. The amorphous aluminosilicates are first depolymerized by alkali activator, and these depolymerized aluminosilicates re-polymerize to form a dense three-dimensional structure (Pozarnsky and McCormick, 1995).

2.1.2. Tannery sludge

Tannery sludge was obtained from a tannery company in Haining, China. The main components of the sludge analyzed via XRF is presented in Table 2. In addition, the total chromium-leaching concentration and total chromium-content of the sludge are 117.9 mg/L and 32,715 mg/kg respectively.

The XRD results for the leather sludge are shown in the Fig. 2. It can be seen from the figure that the content phase in the sludge is mainly $CaCO_3$, with a small amount of SiO_2 also present.

2.1.3. Alkaline activators

The alkaline activators were prepared by dissolving NaOH (AR) in sodium silicate solution (industrial grade; Hangzhou, China). Their SiO_2 mass fraction was 19.4%, their Na_2O mass fraction was 11.3%, and their modulus was 1.8.

2.2. Analytical method

2.2.1. Technological process

Fig. 3 displays the process of generating the tannery sludge based geopolymer. The formula for the geopolymer was determined from the silica/alumina mole ratio and sodium oxide/silica mole ratio; two values defined as A and B, respectively. The masses of metakaolin, tannery sludge, sodium silicate solution, and sodium hydroxide in the reaction system were designated m_1, m_2, m_3, and m_4, respectively. The mass fractions of SiO_2 and Al_2O_3 in the metakaolin were 50.88% and 44.70% respectively. and 4.50% and 3.72%, respectively, in the tannery slydge. According to the mass fraction of sodium silicate in water glass and the modulus of water glass, the mass fractions of silicon dioxide and sodium oxide in water glass were 19.40% and 11.30% respectively. And next the number of moles of each substance can be calculated. Therefore, the equations for A and B are as follows:

$$A = 102 \times (m_1 \times 50.88\% + m_2 \times 4.50\% m_3 \times 19.40\%)/60 \times (m_1 \times 44.70\% + m_2 \times 3.72\%) \tag{1}$$

$$B = 60 \times (m_1 \times 0.28\% + m_2 \times 5.84\% + m_3 \times 11.30\% + m_4 \times 77.50\%)/62 \times (m_1 \times 50.88\% + m_2 \times 4.50\% + m_3 \times 19.40) \tag{2}$$

Table 1
Chemical composition of metakaolin.

Composition	SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	CaO	TiO_2	Na_2O
Percentage (%)	50.88	44.70	1.04	0.27	0.41	0.11	0.28	0.28

Table 2
Chemical composition of tannery sludge.

Composition	SiO_2	Al_2O_3	K_2O	MgO	Fe_2O_3	CaO	Na_2O	Cr_2O_3
Percentage (%)	4.50	3.72	0.20	2.26	28.70	3.32	5.84	4.76

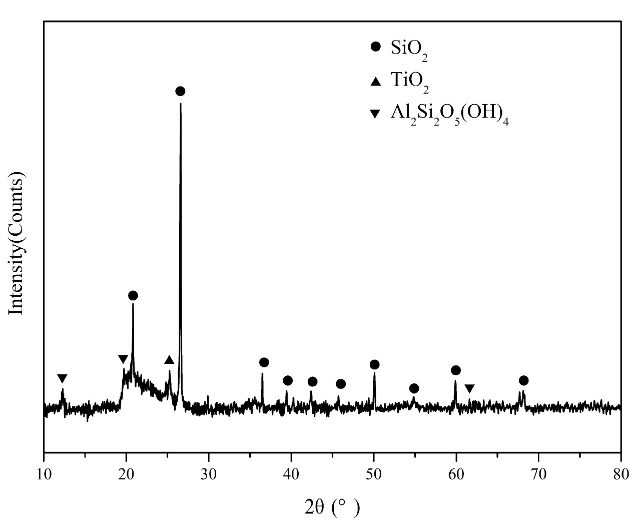

Fig. 1. XRD pattern of metakaolin.

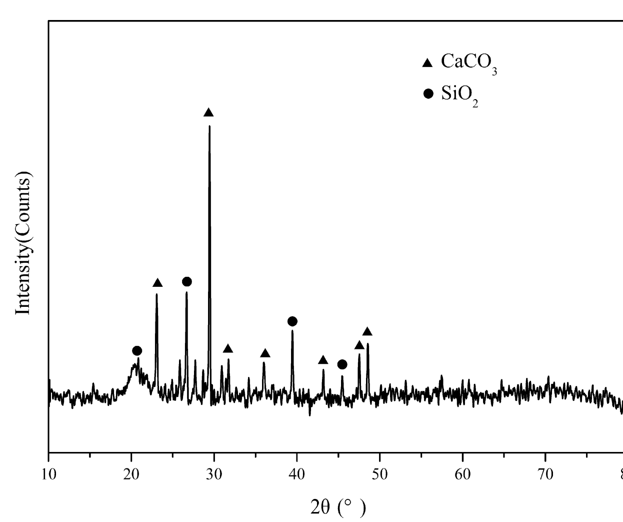

Fig. 2. XRD pattern of tannery sludge.