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Synthesis and characterization of Mn-slag based geopolymer for immobilization of Co



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ABSTRACT

Growth of the nuclear industry has encouraged us to look for techniques to treat large volumes of nuclear waste. ⁶⁰Co is one of the most problematic radioactive wastes in the nuclear industry. In this study, a Mn slag-based geopolymer (MSG) was prepared, which exhibited better Co immobilization performance than the ordinary metakaolin-based geopolymer (MKG). Varying the mass ratio between water glass and NaOH (m_w/m_n) influenced the structure and chemical performance of the MSG samples, which consequently influenced their Co immobilization capacity. The optimized MSG was obtained at an m_w/m_n value of 1.5. After the 7-day leaching test, about 0.20% of the Co was released from MSG, which is less than two-thirds of the MKG sample. The chemical state of Co in the geopolymer matrix was characterized by X-ray photoelectron spectroscopy. Divalent Co remained in the MKG samples, while most of Co ions in MSG samples existed in the trivalent state. These results strongly suggest that divalent Co was oxidized to trivalent Co in the SG matrix, resulting in enhanced Co solidification capacity compared to MKG. The results in this study indicate that the oxidation environment in the MSG played an important role in Co immobilization.

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1. Introduction

Although nuclear energy exhibits many advantages over traditional energy types with regard to the increasing global energy crisis, treating large volumes of nuclear waste has become a critical factor for sustainable development of the industry. ⁶⁰Co is formed by activation of the Co present as an impurity in the metals used in nuclear reactors. It is one of the most problematic radioactive wastes considering solubility, high yield, and long half-life. The best approach to retard mobilization of this radionuclide is to encapsulate it into highly stable low chemically reactive material. Cement-based materials are among the most widely used for encapsulating radioactive wastes. However, the thermal stability and acid corrosion resistance of cement-based materials are

* Corresponding author. E-mail address: yuqq@cug.edu.cn (Q. Yu). relatively low (Malviya and Chaudhary, 2006; Paria and Yuet, 2006; Zhou et al., 2006). Moreover, utilization of other materials, such as glass and resin, is limited by their high cost as well as complex preparation (Li and Wang, 2006).

A geopolymer is a three-dimensional amorphous aluminosilicate inorganic polymer produced by reacting amorphous aluminosilicate with a highly alkaline activating solution. Dissolution and reorganization of the amorphous aluminosilicate occurs during activation. The SiO_4^4 and AlO_4 tetrahedron is randomly interlinked by shared O atoms and forms a rigid three-dimensional network. Because of its excellent mechanical performance, such as compressive strength, acid/alkaline resistance, and heat resistance, geopolymers have become ideal materials for solidifying toxic waste (Al-Zboon et al., 2011; Cheng et al., 2012; Ok et al., 2007). Many studies have focused on the mechanical properties of geopolymers, and reported that changing the curing temperature can significantly affect the strength of the geopolymer based on the types of raw material and the activator (Heah et al., 2012; Hu et al.,







2018, 2019; Nie et al., 2016, 2019).

Attempts to use fly ash and metakaolin-based geopolymers (MKG) to immobilize potentially toxic metals have been reported by several researchers due to their huge production worldwide (Al-Zboon et al., 2011; Cheng et al., 2012; Ge et al., 2017; Kara et al., 2018; Mužek et al., 2014; Pourret, 2018). In these solidification systems, geopolymers exhibit different immobilization efficiencies toward different heavy metals, and the mechanisms vary, Zhang et al. (2008) reported that Pb(II) could be immobilized in geopolymers more effectively compared to Cd(II) and Cr(VI). Wang et al. (2018) determined that solidification of Pb(II), Cd(II), Mn(II), and Cr(III) in a fly ash-based geopolymer occurs by exchange with ions including Na(I) and Ca(II). However, El-Eswed et al. (2017) argued that rather than ion exchange, heavy metals including Pb(II), Cd(II), Cu(II), Th(IV), and U(VI) are immobilized by forming chemical bonds between Si-O⁻ and Al-O⁻. Xu et al. (2017) compared the immobilization efficiency of Sr(II) and MKG with cement and found that Sr(II) showed a higher leaching resistance. They concluded that the geopolymer matrix appeared more compact and dense, which encapsulated Sr more tightly. Limited work has been performed on immobilizing Co(II). Among the studies, metakaolin (MK) is generally used as the starting material. Kara et al. (2018) studied the performance of MKG for Co(II) removal, but the immobilization rate for Co(II) is lower than that of Mn(II). El-Naggar (2014) improved the immobilization effect of ⁶⁰Co by adding blast furnace slag to Egyptian kaolinite. They reported that the compressive strength of the geopolymer was significantly enhanced. As a transition metal, Co(III) possesses much lower solubility than Co(II). The starting material in an oxidizing environment may play a positive role in the Co immobilization process by mechanisms, such as oxidation of Co(II) to Co(III). Unfortunately, no experimental data are available using a starting material other than MK.

The electrolytic Mn metal industry in China has become a dominant supplier in the global Mn market, and produces more than 2×10^6 tons of Mn slag every year (Duan et al., 2010; Liu et al., 2006). Random disposal of this Mn slag (MS) causes serious resource waste as well as environmental problems. Therefore, it is necessary to identify a method to efficiently utilize MS to spare the environment and for sustainability. One of the important ways to recycle MS is to prepare Mn slag-based geopolymer (MSG) materials. However, most studies have focused on the mechanical properties of MSG, and the chemical properties of MSG are still unknown (Wang et al., 2017). MS contains appreciable quantities of aluminosilicate, which makes it available for synthesizing the geopolymer, whereas the remaining Mn oxide in MS provides an ideal oxidative environment. It is theoretically feasible to use MS to prepare the geopolymer to immobilize Co. However, details of the processes by which Co ions are encapsulated into the geopolymer matrix are not yet fully understood, and the preparation conditions have not been optimized.

In this study, the solidification effect of Co(II) by MSG was investigated. A variety of preparation conditions were designed to analyze the factors that influence the structure and properties of MSG. The leaching characteristics of Co from MSG were compared with MKG. The morphology of the geopolymer and the structural properties of the matrix were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FT-IR).

2. Materials and methods

2.1. Materials

MS was received from Leiyang Daji Manganese Industry Co., Ltd.

(Hunan, China). The Mn slag was received in lump form and was crushed in a jaw crusher, then milled with a ball mill to obtain <100 nm powder. Kaolinite was obtained from the Fuhua Kaolinite Co., Ltd. (Guangzhou, China). MK was prepared by calcining kaolinite at 850 °C for 2 h. The chemical composition of the Mn slag was determined by X-ray fluorescence spectrometry (XRF) (AXI-OSmAX, Malvern PANalytical B.V., Almelo, The Netherlands) of the fused discs, as shown in Table S1.

Analytical grade NaOH, CoCl₂ powder, and CH₃COOH were products of Sigma Co. (St. Louis, MO, USA). Water glass was a product of Tianyuan Xing Chemical Industry Co., Ltd. (Wuhan, China).

2.2. Sample preparation

Different geopolymer pastes were prepared by mechanically mixing MS or MK with an alkaline activating solution having a Simodulus of 3. The MSG and MKG mix design is illustrated in Table S2. The geopolymer pastes were cast into molds and vibrated for 2 min to remove entrained air. The prepared molds were kept at 25 ± 0.5 °C in a relative humidity of 90%, and a curing time of 30 days.

2.3. Static leaching test

Static leaching tests were performed to study the leaching of Co from the hardened geopolymer matrices. The leaching process followed the US Environmental Protection Agency's toxicity characteristics leaching procedure (EPA test method #1311). Each prepared sample was ground to obtain a <9.5 mm powder and immersed in 30 mL of 0.1 M CH₃COOH solution (pH = 2.56) with a solid-liquid mass ratio of 1:20. All tested samples were kept in sealed polyethylene bottles, and the leaching test was performed in duplicate in a reciprocating shaker at 25 ± 0.5 °C and 100 rpm. The leachate was sampled every day during the 1 week reaction. The Co released from the geopolymer matrices were monitored by subjecting the supernatants to atomic absorption spectroscopy (TAS-990, Persee Analytics, Auburn, CA, USA) after filtering through a 0.2-µm membrane filter.

2.4. Microstructural and mineralogical characterization

The morphology of the solid samples before and after geopolymerization was investigated by SEM (SU8010; Hitachi, Tokyo, Japan). Powder XRD analyses were carried out on a Bruker AXS D8-Focus diffractometer (Karlsruhe, Germany) equipped with a LynxEye192 detector using Ni-filtered Cu K α radiation ($\lambda = 1.5418$ Å). The diffractometer was operated at a tube voltage of 40 kV and current of 40 mA with a scanning rate of 1°/min at a step of 0.02°. FT-IR spectra of the geopolymer before and after acid leaching were taken on a FT-IR instrument (Vertex 70, Bruker) with KBr disks.

3. Results and discussion

3.1. Synthesis of the MS-based geopolymer

Fig. 1 shows the XRD patterns of MS and MSG. The XRD pattern of MS was characterized by a mixture of crystalline and glassy phases (Fig. 1). A broadly diffused hump corresponding to the glassy or amorphous phase in MS was present at $20-40^{\circ}$ in the 2θ range. The major crystalline phases were quartz, ramsdellite, alabandite, and akermanite. After alkali activation, the center of the amorphous hump was shifted to the high angle range, indicating formation of new amorphous compounds. According to previous reports, this broad hump was generally attributed to amorphous



Fig. 1. X-ray diffraction patterns for the Mn slag (MS) and Mn slag-based geopolymer (MSG).

aluminosilicate gel, which was assumed to be the primary binder phase present in the geopolymer (El-Naggar, 2014; Karaa et al., 2018). Peak intensities of most of the crystalline phases decreased, indicating transformation into amorphous or poorly crystalline gel phases. Some new peaks were observed at 13.9°, 18.7°, 24.2°, 27.4°, and 32.5° (Fig. 1, red symbols), indicating formation of two groups of secondary phases; that is, 1) hydroxides (including doyleite, aluminum hydroxide, aluminum oxide hydrate, and aluminum oxide hydroxide), and 2) carbonates (including magnesite and CaCO₃). The crystalline phases of Co were not detected in any of the MSG samples with added Co, indicating that Co did not form chemical bonds with the aluminosilicate phase of the geopolymer.

The morphology and microstructure of MS and MSG are shown in Fig. 2. The MS was comprised of irregularly shaped blocky particles. The estimated particle size was >1 μ m, and the surface of the particles was smooth (Fig. 2a and b). After polymerization, the surface of most of the particles became diffuse, suggesting formation of a heterogeneous gel. Smaller particles were more diffused than bigger particles. This result indicates that the reaction occurred at the surface boundary and inner crust of a crack. A small amount of plate-like particles was observed on MSG, suggesting formation of secondary crystallites (Fig. 2c and d). This secondary phase was also observed in the XRD analysis. Acid treatment did not change the morphology of any of the samples (Fig. 2e and f). Some fractions of the plate-like secondary phase were preserved even after acid leaching.

The MS and MSG FT-IR spectra are shown in Fig. 3. The broad band between 3,250 and 3,750 cm⁻¹ and the sharp peak at around 1,640 cm⁻¹ were attributed to –OH stretching vibrations. The peaks at about 1,000 cm⁻¹ were attributed to the asymmetric stretching vibrations of Si–O-T (T = Si or Al). The bands between 500 and 800 cm⁻¹ were attributed to Al–O–Si vibrations, and the bands between 450 and 470 were attributed to Si–O–Si bending vibrations (Ge et al., 2015, 2017; Kara et al., 2018). Three major differences were observed in the samples before and after geopolymerization: 1) the intensity of the absorption band for –OH stretching and bending vibrations of CO_3^2 appeared at about 1,380–1,430 cm⁻¹ after geopolymerization, and were ascribed to

the reaction of free ions with atmospheric CO₂ (Frias et al., 2006; Lecomte et al., 2006). 3) The characteristic signal of Si–O–Si symmetric stretching at 795 cm⁻¹ disappeared after geopolymerization, and the Si–O–T band at about 1,000 cm⁻¹ was right shifted, suggesting dissolution of the original Si–O–Si bond and formation of a Si–O–Al network during geopolymerization.

3.2. Optimizing the synthetic conditions

The XRD patterns of the MSG samples with different alkali activator dosages on formation of the geopolymer are presented in Fig. 4. Some peaks assigned to the secondary phase clearly increased with the decrease in the water glass/NaOH mass ratio (m_w/m_n) , (Fig. 4, black symbols), while changes in the original phases were relatively small (Fig. 4, white symbols).

To better understand the changes in crystalline structure with alkali activator dosage, the expanded XRD patterns in the 2θ range of 27–34° for the samples are plotted in Fig. 5. As one of the main crystalline phases in MS, the content of akermanite was not affected by the alkaline activator dosage (Fig. 5), suggesting that akermanite may not be involved in the dissolution-reorganization process during geopolymerization due to its low hydration activity. Magnesite and CaCO₃ were formed as the m_w/m_n value decreased (Fig. 5). It is known that higher alkalinity in the activating solution accelerates dissolution of aluminosilicate. Ions such as Mg²⁺ and Ca²⁺ released from the matrix of the raw material have a greater chance of reacting with atmospheric CO₂ to form carbonates. Aluminum oxide hydrate started to form until the m_w/m_n value was <1.5 (Fig. 5). After dissolving the aluminosilicate, the Al³⁺ released from MS reacted with SiO_3^{2-} in water glass to form Al-O-Si oligomers. When the water glass/NaOH mass ratio is very low, the amount of SiO_3^{2-} is insufficient to form the Al–O–Si matrix. Thus, the excess Al^{3+} reacted with NaOH to form the hydroxide. Compared with the m_w/m_n value, the mass ratio between the alkali-activator and MS (m_{Alk}/m_{MS}) showed less of an effect on the crystalline phase of the MSG samples. The XRD patterns of the MSG samples before and after acid leaching were similar (Fig. S1), suggesting high acid resistance.

The FT-IR spectra of the MSG samples with different alkali activator dosages were collected to determine the changes in the chemical bonds in both the crystalline and amorphous phases, and the MS spectrum was plotted for comparison (Fig. 6). As the m_w/m_n value decreased from 9.0 to 1.0, the absorption peaks for MSG at ca. 1,000 cm⁻¹ were gradually right-shifted. Moreover, the vibrating region at 450-800 cm⁻¹ changed from a smooth curve into absorption bands with several characteristic peaks. These peaks were attributed to the asymmetric stretching vibrations of Si-O-T (T = Si or Al). Although no significant differences were observed in the XRD patterns for samples with m_w/m_n values > 2.3, the changes in the FT-IR spectra clearly show that the amorphous phase reorganized and that the Si-O-Al oligomers formed gradually. The intensity of the CO_3^{2-} peak at 1,385 cm⁻¹ decreased as the m_w/m_n value decreased, and a new peak at 1,425 cm⁻¹ gradually appeared (Fig. 6). Increased intensity at $1,425 \text{ cm}^{-1}$ could be explained by the correlation with the XRD results shown in Fig. 4. Carbonates (such as magnesite and CaCO₃) were formed as the m_w/m_n value decreased. Accordingly, the observed changes were ascribed to transformation of the surface adsorbed/amorphous CO_3^{2-} into crystallized carbonates. The FT-IR data combined with the XRD results suggest that the activating solution with a low m_w/m_n value could accelerate reorganization of Si-O-Al oligomers to form an ordered structure. On the other hand, secondary phases, such as hydroxide and carbonate formed, as the m_w/m_n value was very low.

The FT-IR spectra of the MSG samples after leaching with 0.1 M CH₃COOH solution are plotted in Fig. S5. The peak at 1,385 cm⁻¹



Fig. 2. Scanning electron micrographs of (a)-(b) Mn slag (MS), (c)-(d) Mn slag-based geopolymer (MSG) before acidic leaching, and (e)-(f) MSG after acidic leaching.

disappeared, whereas the peak at $1,425 \text{ cm}^{-1}$ remained. After the acid treatment, surface adsorbed/amorphous CO_3^{2-} was reacted with protons to form CO₂. Part of the carbonate located in the crystalline structure of the secondary phase possessed higher stability toward proton attack. This result concurs with the SEM observations that a plate-like secondary phase remained after the acid treatment. The broad feature at about 1,000 cm⁻¹ for samples with a high m_w/m_n value disappeared after the acid treatment, and a sharp peak was observed in all samples. This result indicates that the ordered structure of the Si–O–Al network possesses a much higher acid resistance.

3.3. Leaching characteristics of Co from geopolymer matrices

The variations in the leached fraction of Co from 15 MSG

samples are shown in Fig. 7. The leaching behavior can be described as rapid release of Co within the first day followed by a much slower leaching rate during the remaining 6 days. The rapid release of Co on the first day originated from the fraction located on the surface of the MSG particles. The particles of all MSG samples were similar. Therefore, a similar leaching rate was observed during this period. After 1-day of leaching, Co located in deeper places gradually diffused into solution. Consequently, the leaching rate of Co was highly related with its pathway inside the MSG particles. The leaching rate of Co decreased as the m_w/m_n value increased within the range of 9.0 to 1.5. It has been reported that acid attack causes dealumination and depolymerization of the geopolymer structure (Bakharev, 2005; Mehta and Siddique, 2017). An activating solution with a low m_w/m_n value facilitates reorganization of the Si–O–Al oligomers to form an ordered structure, which possesses higher



Fig. 3. Fourier transform infrared spectra of the Mn slag (MS) and Mn slag-based geopolymer (MSG).

stability against an acid attack. When the m_w/m_n value of the activating solution was <1.5, the amount of Co released increased. According to the XRD and FT-IR analyses, the amounts of hydroxides and carbonates increased as the m_w/m_n value decreased (Figs. 4 and 6). These secondary phases dissolved after exposure to an acetic acid solution for 7 days, and the Co ions located in the crystal were released into solution. The leaching fractions of Co for the MSG samples with a m_{Alk}/m_{MS} value of 0.7 and 0.75 were similar, and slightly increased for MSG samples with a m_{Alk}/m_{MS} value of 0.8. It has been reported that geopolymer prepared with a different liquid-solid ratio may result in varying microstructures (Hu et al., 2018, 2019; Mu et al., 2017). In the present study, the liquid-solid ratio varied slightly for the MSG samples with different m_{Alk}/m_{MS} values, which may further affect the immobilization results. The leaching behavior of MKG was also plotted for comparison. The leaching rate of Co from MKG was nearly two times higher than that from MSG on the first day. During all testing periods, the amount of Co released from MKG was much higher than that from MSG.

Fig. 7d shows the fraction of Co released from the MSG samples after 7 days of leaching. The leachability of Co from all MSG samples was <0.35%, demonstrating good leaching resistance. The m_w/m_n value had the greatest effect on the leaching concentration of Co. The optimized MSG was obtained at an m_w/m_n value of 1.5, and a m_{Alk}/m_{MS} value of 0.7 showed that about 0.20% of the Co was released from MSG after the 7-day leaching test. More than 0.34% of Co was released from MKG after the 7-day reaction, which is more than 1.5 times higher than that from MSG.

We used X-ray photoelectron spectroscopy (XPS) to determine the chemical state of Co in the MSG and MKG matrix. As shown in Fig. 8, the Co 2p XPS spectra for MKG before and after acidic leaching were similar. Before acid leaching, peaks for Co $2p_{1/2}$ and



Fig. 5. Expanded X-ray diffraction patterns in the range of $2\theta = 27-34^{\circ}$ for the Mn slagbased geopolymer (MSG) samples before acid leaching. Symbols: \blacktriangle Aluminum oxide hydrate; \blacksquare CaCO₃; \triangle Akermanite; \blacklozenge Magnesite.



Fig. 4. X-ray diffraction patterns of the Mn slag-based geopolymer (MSG) samples before acid leaching. Symbols: ▲ Aluminum (hydro)oxides; ○ Alabandite; Quartz; ■ Carbonates; △ Akermanite.



Fig. 6. The Fourier transform infrared spectra of the Mn slag-based geopolymer (MSG) samples before acid leaching.

Co $2p_{3/2}$ were observed at 797.3 eV and 781.2 eV, respectively. After acid leaching, these peaks were observed at 797.2 eV and 781.2 eV, respectively. Clear satellite peaks were observed on the high energy

side, and the binding energies between the Co $2p_{1/2}$ and Co $2p_{3/2}$ peaks were 16.1 eV and 16.0 eV for MKG before and after acid leaching, respectively. These results indicate that Co(II) exclusively



Fig. 7. The leaching kinetics of Co for the (a) Mn slag-based geopolymer (MSG)1-MSG5, (b) MSG6-MSG10, (C) MSG11-MSG15, and (d) comparison of the leaching concentration of Co for MSG samples and the metakaolin-based geopolymer (MKG).



Fig. 8. Co2p X-ray photoelectron spectroscopy (XPS) spectra of (a, b) the Mn slag-based geopolymer (MSG), and (c, d) the metakaolin-based geopolymer (MKG) samples (a, c) before and (b, d) after acid leaching.

exists in the MKG samples. Clear differences were observed in the MSG samples. Sharp peaks for Co $2p_{1/2}$ and Co $2p_{3/2}$ were observed at 795.0 eV and 780.0 eV, respectively. No satellite peaks were observed. The binding energy between the two peaks was 15.0 eV, which is consistent with those of CoOOH (Crowther et al., 1983). This result suggests that Co(III) mainly exists in the MSG samples. According to the XRD results, ramsdellite, a strong Co(II) oxidant, was present as a crystalline phase in the MSG sample. During polymerization, Co(II) adsorbed on the surface of the MSG particles was oxidized to Co(III). Co(III) possesses higher resistance against acid leaching due to its lower solubility compared with Co(II). As a result, Co immobilized by the MSG matrix exhibited higher stability than that of MKG. After leaching with the acetic acid solution for 7 days, the binding energy of the two peaks shifted to the high energy side. The binding energy between the two peaks was 15.8 eV, which was between the values of Co(III) $(15 \pm 0.1 \text{ eV})$ and Co(II) $(15.9 \pm 0.1 \text{ eV})$ (Crowther et al., 1983). Moreover, small satellite peaks appeared on the high energy side. This result indicates that a fraction of the Co(III) was reduced to Co(II) after acidic leaching. The XPS results clearly demonstrate that MSG possessed a higher capacity for immobilizing Co because of its oxidative reactivity.

3.4. Immobilization of Co by MSG

Co immobilized by MSG exhibited higher resistance against acid leaching compared to that of MKG. According to the XPS analysis, Co immobilized by MSG was mainly present in a trivalent state, while divalent Co was the main species in MKG. The XPS and leaching test results clearly show that the oxidation reaction effectively enhanced immobilization of Co by the MSG matrix. Combined with the information from the XRD, FT-IR, and XPS analyses, the immobilization mechanism of Co by MSG is discussed. Amorphous aluminosilicate dissolves in an alkaline environment. Crystalline phases, including ramsdellite, were released and reacted with Co(II), and the reaction is depicted as Eq. (1):

$$\operatorname{Co(II)} + 2\operatorname{Mn(IV)O_2} + \operatorname{H_2O} \to \operatorname{Co(III)} + \operatorname{Mn(III)_2O_3} + 2\operatorname{OH^-}$$
(1)

Two OH^- were generated in this reaction, which further enhanced dissolution of the amorphous aluminosilicate. In the following polycondensation process, the Al combined with a silicate molecule to generate a -O-Si-O-Al-O- skeleton structure. To balance the negative charge of tetrahedrally coordinated AlO_4^- , Co was easily adsorbed and/or immobilized on the geopolymer structure. In addition, physical fixation and precipitation may also contribute to immobilize Co for encapsulation into the geopolymer matrix.

4. Conclusion

In this study, we compared the performance of immobilizing Co with a Mn slag-based geopolymer and an ordinary metakaolinbased geopolymer. The m_w/m_n value of the alkali activator greatly affected the structure and chemical performance of the MSG samples. An activating solution with a low m_w/m_n value accelerated reorganization of Si-O-Al oligomers to form an ordered structure, whereas the amounts of hydroxides and carbonates increased as the m_w/m_n value decreased. Based on the leaching concentration, the optimum conditions for preparing MSG were m_w/m_n value of 1.5 and a m_{Alk}/m_{MS} value of 0.7, and about 0.20% of the Co was released from the optimized MSG after the 7-day leaching test. More than 0.34% of Co was released from MKG after the 7-day reaction, which is more than 1.5 times higher than that from MSG. The oxidation state of Co ions in MSG plays an important role in Co mobility. The oxidation reaction effectively enhanced immobilization of Co by the MSG matrix.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2019.06.149.

References

- Al-Zboon, K., Al-Harahsheh, M.S., Hani, F.B., 2011. Fly ash-based geopolymer for Pb removal from aqueous solution. J. Hazard Mater. 188 (1–3), 414–421.
- Bakharev, T., 2005. Resistance of geopolymer materials to acid attack. Cement Concr. Res. 35 (4), 658–670.
- Cheng, T.W., Lee, M.L., Ko, M.S., Ueng, T.H., Yang, S.F., 2012. The heavy metal adsorption characteristics on metakaolin-based geopolymer. Appl. Clay Sci. 56, 90–96.
- Crowther, D.L., Dillard, J.G., Murray, J.W., 1983. The mechanisms of Co(II) oxidation on synthetic birnessite. Geochem. Cosmochim. Acta 47 (8), 1399–1403.
- Duan, N., Fan, W., Changbo, Z., Chunlei, Z., Hongbing, Y., 2010. Analysis of pollution materials generated from electrolytic manganese industries in China. Resour. Conserv. Recycl. 54 (8), 506–511.
- El-Eswed, B.I., Aldagag, O.M., Khalili, F.I., 2017. Efficiency and mechanism of stabilization/solidification of Pb(II), Cd(II), Cu(II), Th(IV) and U(VI) in metakaolin based geopolymers. Appl. Clay Sci. 140, 148–156.
- El-Naggar, M.R., 2014. Applicability of alkali activated slag-seeded Egyptian Sinai kaolin for the immobilization of ⁶⁰Co radionuclide. J. Nucl. Mater. 447, 15–21.
- Frias, M., Rojas, M.I.S.D., Santamaría, J., Rodríguez, C., 2006. Recycling of silicomanganese slag as pozzolanic material in Portland cements: basic and engineering properties. Cement Concr. Res. 36 (3), 487–491.
- Ge, Y., Cui, X., Kong, Y., Li, Z., He, Y., Zhou, Q., 2015. Porous geopolymeric spheres for removal of Cu(II) from aqueous solution: synthesis and evaluation. J. Hazard Mater. (283), 244–251.
- Ge, Y., Cui, X., Liao, C., Li, Z., 2017. Facile fabrication of green geopolymer/alginate hybrid spheres for efficient removal of Cu(II) in water: batch and column studies. Chem. Eng. J. 311, 126–134.
- Heah, C.Y., Kamarudin, H., Mustafa Al Bakri, A.M., Bnhussain, M., Luqman, M., Khairul Nizar, I., Ruzaidi, C.M., Liew, Y.M., 2012. Study on solids-to-liquid and alkaline activator ratios on kaolin-based geopolymers. Constr. Build. Mater. 35, 912–922.
- Hu, Wei, Nie, Qingke, Huang, Baoshan, Xiang, Shu, He, Qiang, 2018. Mechanical and

microstructural characterization of geopolymers derived from red mud and fly ashes. J. Clean. Prod. https://doi.org/10.1016/j.jclepro.2018.03.086 (2018).

- Hu, W., Nie, Q., Huang, B., Shu, X., 2019. Investigation of the strength development of cast-in-place geopolymer piles with heating systems. J. Clean. Prod. https:// doi.org/10.1016/j.jclepro.2019.01.155.
- Kara, I., Tunc, D., Sayin, F., Akar, S.T., 2018. Study on the performance of metakaolin based geopolymer for Mn(II) and Co(II) removal. Appl. Clay Sci. 161, 184–193.
- Lecomte, I., Henrist, C., Liégeois, M., Maseri, F., Rulmont, A., Cloots, R., 2006. (Micro)structural comparison between geopolymers, alkali-activated slag cement and Portland cement. J. Eur. Ceram. Soc. 26 (16), 3789–3797.
- Li, J., Wang, J., 2006. Advances in cement solidification technology for waste radioactive ion exchange resins: a review. J. Hazard Mater. 135 (1–3), 443–448.
- Liu, T.J., Tan, Z.J., Liao, S.H., 2006. An Analyse of Trend of EMM Industry. Chinas Manganese Industry.
- Malviya, R., Chaudhary, R., 2006. Factors affecting hazardous waste solidification/ stabilization: a review. J. Hazard Mater. 137 (1), 267.
- Mehta, A., Siddique, R., 2017. Sulfuric acid resistance of fly ash based geopolymer concrete. Constr. Build. Mater. 146, 136–143.
- Mu, S., Liu, J., Lin, W., Wang, Y., Liu, J., Shi, L., Jiang, Q., 2017. Property and microstructure of aluminosilicate inorganic coating for concrete: role of water to solid ratio. Constr. Build. Mater. 148, 846–856.
- Mužek, M.N., Svilović, S., Zelić, J., 2014. Fly ash-based geopolymeric adsorbent for copper ion removal from wastewater. Desalination Water Treat. 52 (13–15), 2519–2526.
- Nie, Q., Hu, W., Ai, T., Huang, B., Shu, X., He, Q., 2016. Strength properties of geopolymers derived from original and desulfurized red mud cured at ambient temperature. Constr. Build. Mater. 125, 905–911.
- Nie, Q., HuW, Huang, B., Shu, X., He, Q., 2019. Synergistic utilization of red mud for flue-gas desulfurization and fly ash-based geopolymer preparation. J. Hazard Mater. https://doi.org/10.1016/j.jhazmat.2019.02.059.
- Ok, Y.S., Yang, J.E., Zhang, Y., Kim, S., Chung, D., 2007. Heavy metal adsorption by a formulated zeolite-Portland cement mixture. J. Hazard Mater. 147 (1), 91–96.
- Paria, S., Yuet, P.K., 2006. Solidification/stabilization of organic and inorganic contaminates using Portland cement: a literature review. Environ. Rev. 14 (4), 217–255.
- Pourret, O., 2018. On the necessity of banning the term "heavy metal" from the scientific literature. Sustainability 10 (8), 2879.
- Wang, Y., Han, F., Zhao, S., Mu, J., 2017. Preparation and characterization of manganese slag and fly ash-based geopolymer. MATEC Web Conf. 130, 04006.
- Wang, Y., Han, F., Mu, J., 2018. Solidification/stabilization mechanism of Pb(II), Cd(II), Mn(II) and Cr(III) in fly ash based geopolymers. Constr. Build. Mater. 30 (160), 818–827.
- Xu, Z., Jiang, Z., Wu, D., Peng, X., Xu, Y., Li, N., Qi, Y., Li, P., 2017. Immobilization of strontium-loaded zeolite A by metakaolin based-geopolymer. Ceram. Int. 43 (5), 4434–4439.
- Zhang, J., Provis, J.L., Feng, D., van Deventer, J.S., 2008. Geopolymers for immobilization of Cr(VII), Cd(II), and Pb(II). J. Hazard Mater. 157 (2–3), 587–598.
- Zhou, Q., Milestone, N.B., Hayes, M., 2006. An alternative to Portland Cement for waste encapsulation-the calcium sulfoaluminate cement system. J. Hazard Mater. 136 (1), 120–129.