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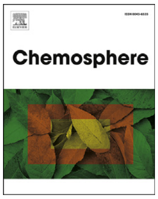

A simultaneous stabilization and solidification of the top five most toxic heavy metals (Hg, Pb, As, Cr, and Cd)

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HIGHLIGHTS

- A new CBPC-type stabilization/solidification (S/S) process was developed.
- The new process effectively and simultaneously stabilized Hg, Pb, As, Cr, and Cd.
- $FeCl_2$, a stabilizer, was highly effective in the stabilization of As and Cr.
- The TCLP values of all the final products were below the UTS values.
- The compressive strengths of all the final products met the US NRCS requirements.

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ABSTRACT

A novel chemically bonded phosphate ceramic (CBPC) binder was developed for the simultaneous treatment of the top five most toxic heavy metals (Hg, Pb, As, Cr, and Cd). Various CBPC binders were synthesized and tested, and their toxicity characteristic leaching procedure (TCLP) values were obtained. A magnesium/calcium-potassium phosphate ceramic binder with $FeCl_2$ (M/C-KP-$FeCl_2$) simultaneously stabilized multiple heavy metals. The TCLP value of the final product for industrial waste (IW) treatment using the M/C-KP-$FeCl_2$ technology was well below the Universal Treatment Standard (UTS). Additionally, the compressive strength of the final product was below the US Nuclear Regulatory Commission Standard.

1. Introduction

Considerable interest in treatment processes for mercury (Hg)-containing waste has arisen since the Minamata Convention on Mercury (Larson, 2014; Mackey et al., 2014; Yang, 2015) was signed in October 2013, and attention has also been focused on other heavy metals, such as Pb, Cd, and As. New regulations have already been established for heavy metals in several countries (Järup, 2003; Duruibe et al., 2007; Nagajyoti et al., 2010). For example, the United States manages hazardous waste according to Land Disposal Restrictions (LDRs; 40 CFR Part 268), which regulate the ways in which wastes are managed to render them physically and chemically suitable for soil landfill (Sharma and Lewis, 1994; Voigt et al., 1996; Crannell et al., 2000; Järup, 2003). Wastes are categorized as hazardous when the toxicity characteristic leaching procedure (TCLP) values of the heavy metals (Hg, Pb, As, Cr, and Cd) are above the standard set in the Resource Conservation and Recovery Act (RCRA: Hg = 0.2 mg/L, Pb = 5.0 mg/L, As = 5.0 mg/L, Cr = 5.0 mg/L, Cd = 1.0 mg/L) (Barthel and Edwards, 2004). Hazardous wastes must be handled with intermediary management methods, such as stabilization/solidification (S/S) and/or thermal treatment, until the TCLP value of the treated product is below the Universal Treatment Standard (UTS: Hg = 0.025 mg/L, Pb = 0.75 mg/L, As = 5.0 mg/L, Cr = 0.65 mg/L, Cd = 0.11 mg/L) (Barthel and Edwards, 2004; Nagajyoti et al., 2010).

S/S technology converts industrial waste (IW) contaminated with hazardous materials into a stabilized form through physical and chemical treatment (Singh et al., 1997; Wagh et al., 1998;

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Fuhrmann et al., 2002; Dermatas and Meng, 2003; Wagh, 2004; Paria and Yuet, 2006; Barnett et al., 2009; Hagemann, 2009; Beeghly and Schrock, 2010; Anastasiadou et al., 2012). The chemically bonded phosphate ceramic (CBPC) technology is used for the S/S of hazardous waste. In particular, CBPC materials consisting of magnesium potassium phosphate (MKP) ceramics are currently the most popular for treating Hg-containing wastes (Liu et al., 2008; Randall and Chattopadhyay, 2010; Cho et al., 2014a, 2014b). However, MKP technology suffers from premature solidification before the complete diffusion of the waste due to the fast binder reaction (Wei et al., 2010; Formosa et al., 2012; Cho et al., 2014a, 2014b). Recently, Lee and co-workers introduced a new CBPC technology using calcium-sodium phosphate (CNP) (Cho et al., 2014a, 2014b). The existing compressive strength of the MKP technology and the stabilization and solidification performance of MKP with respect to the TCLP are maintained with the CNP method, but the reaction time can be increased from 10 to 15 min to a maximum of 35 min. The advantage of this increased reaction time is that the solidifying material and binder have adequate time to mix. Using CNP is an effective technology because the material does not require calcination at high temperature or additional additives to reduce the reaction time, in contrast to the MKP process (Cho et al., 2014a, 2014b).

In this study, MKP, CNP, magnesium/calcium-potassium phosphate (M/C-KP), magnesium/calcium-sodium phosphate (M/C-NP), magnesium-potassium/sodium phosphate (M-K/NP), and calcium-potassium/sodium phosphate (C-K/NP) ceramic binders were prepared, and their abilities to stabilize the top five most toxic heavy metals (Hg, Pb, As, Cr, and Cd) were tested. Additionally, the effect of a stabilization reagent (FeO, $FeSO_4$, and $FeCl_2$) on the leaching characteristics of the compounds was investigated. Finally, IWs containing heavy metals were stabilized and solidified using the binders listed above to determine the best treatment parameters.

2. Experimental

2.1. Preparation of the CBPC binder (spiked with heavy metals)

In this study, MKP, CNP, M/C-KP, M/C-NP, M-K/NP, and C-K/NP ceramic binders were prepared by combining two metallic oxides (MgO and CaO) and two phosphates (KH_2PO_4 and Na_2HPO_4), and the binders were then tested.

CBPC technology is used in a method that stabilizes and solidifies hazardous wastes by forming a ceramic through acid-base phosphorylation between the metallic oxides and phosphates in the presence of water. CBPC binders were synthesized using reagent-grade MgO, CaO, KH_2PO_4, and Na_2HPO_4 (Samchun Pure Chemical Co., Ltd., Korea) in the molar ratios shown in Table 1.

Five moles of diluted stock solutions of each hazardous heavy metal, prepared using de-ionized (DI) water, was added during the synthesis of each blank binder. The metallic ions contained in each binder are listed in the following table. The top five most hazardous trace metals (Hg, Pb, As, Cr, and Cd) were diluted to 200 mg/kg in the solutions to verify their chemical stability as ions. Many iron compounds are used as stabilization additives for various heavy metals (Voigt et al., 1996; Crannell et al., 2000; Halim et al., 2003; Cheng et al., 2009; Aucott et al., 2010; Shafiquzzaman et al., 2010; Nicklaus et al., 2014; Zhang et al., 2015), and FeO, $FeSO_4$, and $FeCl_2$ were added to stabilize As and Cr in this study. The ceramic product was synthesized after adding 5 wt% of the total binder weight with each heavy metal ratio.

Table 1
Base materials used for the CBPC binders.

CBPC Binder	Metal Oxide (mol)		Phosphate Salt (mol)	
	MgO	CaO	K_2HPO_4	Na_2HPO_4
MKP	1.0	–	1.0	–
CNP	–	1	–	1.0
M/C-KP	0.5	0.5	1.0	–
M/C-NP	0.5	0.5	–	1.0
M-K/NP	1.0	–	0.5	0.5
C-K/NP	–	1.0	0.5	0.5

2.2. S/S of the IWs

This study examined the S/S of IWs (IW#1 and IW#2) using an M/C-KP-$FeCl_2$ binder, which exhibited the highest stabilization ratio for many heavy metals. When the IW was not contained, a sol-gel synthesis reaction was induced using 5 mol of DI water; however, when the waste was added, the amount of DI water was insufficient, which led to an imperfect mixing of the binder and IW. In contrast, when the amount of H_2O was much greater than required, it was difficult to develop a crystallized solid because the physical integrity of the final product was affected by insufficient gel condensation. Therefore, when the IW was stabilized and solidified, the S/S process utilized materials synthesized with varying amounts, depending on the ratio of the binder to IW.

The IW was mixed at ratios of 25, 50, and 100% based on the solidified binder weight. Additionally, $FeCl_2$ was used as a stabilization reagent in the relevant binders and in the S/S process in amounts of 0.5, 2, and 5 wt% of the binder weight to 1) determine the optimal content of the stabilization reagent and 2) compared the difference of physical properties occurring due to the addition of $FeCl_2$.

2.3. Characteristics of the IWs

Two IWs (IW#1 and IW#2) containing the top five most toxic heavy metals (Hg, Pb, As, Cr, and Cd) were sampled and tested in this study. IW#1 was a wastewater treatment sludge produced during zinc production. IW#2 was fly ash produced during waste incineration. The IWs used in this study were analyzed for their heavy metal contents and the TCLP values of the heavy metals. The Hg content in the industrial sludge was determined according to US EPA method 7471B using a cold vapor atomic absorption (CVAA) Hg analyzer (RA-915$^+$/RP-91, Lumex Ltd., Russia) (Liu et al., 2008; Hagemann, 2009; Cho et al., 2014a, 2014b). The contents of the other heavy metals (Pb, As, Cr, and Cd) were determined according to US EPA method 3051 using inductively coupled plasma-optical emission spectrometry (ICP-OES: Optima 7300 DV, PerkinElmer Inc., USA) (Duruibe et al., 2007; Nagajyoti et al., 2010; Wang et al., 2015).

The TCLP values were determined according to US EPA method 1311. The Hg concentration in the TCLP extraction fluid was measured according to US EPA method 7470A using the Hg analyzer. The concentrations of the other hazardous heavy metals (Pb, As, Cr, and Cd) in the TCLP extraction fluid were measured according to US EPA method 200.7 using ICP-OES. Only the IWs with TCLP values higher than the RCRA standards ($Hg = 0.2$ mg/L, $Pb = 5.0$ mg/L, $As = 5.0$ mg/L, $Cr = 5.0$ mg/L, and $Cd = 1.0$ mg/L) were further stabilized and solidified.

2.4. TCLP test

The TCLP tests were conducted to determine the leaching value of the final product using the accredited testing method, US EPA method 1311. The extraction solution in this study consisted of fluid #1. The extraction was performed by first mixing 2 L of the extraction solution with 100 g of a homogenized sample, which had been milled to less than 9.5 mm, in a high-density polyethylene