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Influence of lead on stabilization/solidification by ordinary Portland cement and magnesium phosphate cement

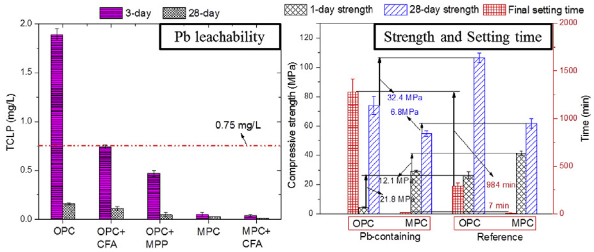
Yan-Shuai Wang, Jian-Guo Dai**, Lei Wang, Daniel C.W. Tsang*, Chi Sun Poon

Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hong Kong, China

HIGHLIGHTS

- Pb mainly delays the induction period during OPC hydration.
- Pb incorporation reduces strength of OPC-based S/S cubes by 30.4%.
- MKPC is a more efficient inorganic binder for Pb S/S with low leachability.
- MKPC-based S/S depends on phosphate precipitation and struvite-K encapsulation.

GRAPHICAL ABSTRACT



Influence of Pb on S/S: OPC: Large MPC: Small

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ABSTRACT

Inorganic binder-based stabilization/solidification (S/S) of Pb-contaminated soil is a commonly used remediation approach. This paper investigates the influences of soluble Pb species on the hydration process of two types of inorganic binders: ordinary Portland cement (OPC) and magnesium potassium phosphate cement (MKPC). The environmental leachability, compressive strength, and setting time of the cement products are assessed as the primary performance indicators. The mechanisms of Pb involved in the hydration process are analyzed through X-ray diffraction (XRD), hydration heat evolution, and thermogravimetric analyses. Results show that the presence of Pb imposes adverse impact on the compressive strength (decreased by 30.4%) and the final setting time (prolonged by 334.7%) of OPC, but it exerts much less influence on those of MKPC. The reduced strength and delayed setting are attributed to the retarded hydration reaction rate of OPC during the induction period. These results suggest that the OPC-based S/S of soluble Pb mainly depends on physical encapsulation by calcium-silicate-hydrate (C—S—H) gels. In contrast, in case of MKPC-based S/S process, chemical stabilization with residual phosphate (pyromorphite and lead phosphate precipitation) and physical fixation of cementitious struvite-K are the major mechanisms. Therefore, MKPC is a more efficient and chemically stable inorganic binder for the Pb S/S process.

1. Introduction

Plumbism is a serious public health concern, especially during one's childhood when the central nervous system is vulnerable to the Pb infection that leads to the cognitive disorder. One of the primary sources of Pb exposure is the Pb-contaminated soil, in which the soluble Pb species are regarded as a major harmful form

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* Corresponding author.
** Corresponding author.
E-mail addresses: cejgdai@polyu.edu.hk (J.-G. Dai), dan.tsang@polyu.edu.hk (D.C.W. Tsang).

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(Beiyuan et al., 2017). It jeopardizes not only the human health as described above but also the environment by contaminating surface water and groundwater resources. It is therefore imperative to implement low-cost and effective remediation technologies to cope with the soil before the soluble Pb species are released. In general, stabilization/solidification (S/S) of the heavy metals in contaminated soil is commonly used remediation technologies. The attributes of low cost and short project duration popularize the cement-based S/S treatment in densely populated cities, which can accomplish physical encapsulation and chemical fixation of hazardous substances. The physical solidification aims to improve the engineering properties (e.g., low permeability and high bearing capacity) of the solidified soil, while the chemical stabilization focuses on the chemical alteration of contaminants so that their leachability is eliminated or minimized. Recent studies (Du et al., 2016; Wang et al., 2015a, 2015b, 2016) further suggest that S/S treatment can also recycle the contaminated soil/sediment into an eco-friendly construction materials as site formation fill materials (HK EPD, 2011) or as non-load-bearing masonry unit (ASTM, 2011).

The S/S process encapsulates the contaminated soils, and reduces the bioavailability, leachability, and mobility of hazardous species (e.g., soluble Pb). Previous literature indicated that the S/S of contaminated soils was widely realized by using economical hydraulic binders, such as ordinary Portland cement (OPC) (Paria and Yuet, 2006), lime (Wang et al., 2015a), coal fly ash (CFA) (Wang et al., 2015b), red mud (Zhang et al., 2016), ground granulated blast furnace slag (Wang et al., 2015a), and incineration sewage sludge ash (Li and Poon, 2017). Alkali-activated high-calcium materials (Komnitsas et al., 2013; Huang et al., 2016) and geopolymer binders (e.g., alkali-activated low-calcium aluminoslicate minerals) (Al-harahsheh et al., 2015) with eco-friendly attributes and thermal stability have also been explored to form hydration products of C–S–H gels for the S/S of heavy metals. The heavy metals could be fixed in the molecular network formed during the geopolymerization, either chemically embedded into the crystalline structure by substitution or physically entrapped by the surrounding network (Waijarean et al., 2017; Zheng et al., 2010). In addition, the alkali environment can transform the heavy metals to barely soluble hydroxides.

However, two main disadvantages of the high-alkali binders for soil remediation were also reported: (1) during the hydration of hydraulic binders, the metal-containing (e.g., Pb) hydrate phases precipitate a complex mixture (containing PbO, $Pb(OH)_2$, mixed salt $PbOPb(OH)_2$, etc.), which may accumulate and form an impervious coating and interfere the cement hydration (Cartledge et al., 1990; Wang et al., 2015b); (2) the high-alkali cementitious materials, when subject to chronic/severe acidic conditions (e.g., acid rain, sulphate attack, and carbonation), are likely to leach the heavy metals due to the performance deterioration of binders (Du et al., 2012, 2014a; Li et al., 2015). Considering the amphoteric nature, these Pb-containing hydroxides encountering high concentration of OH^- dissolve and generate the soluble $Pb(OH)_3^-$, accounting for the dissolution and re-precipitation of lead salts throughout the cement hydration process (Cartledge et al., 1990; Park et al., 2011).

A typical magnesium phosphate cement (MPC), i.e., magnesium potassium phosphate cement (MKPC), is proposed here for the immobilization of soluble Pb. The hydration of MKPC is based on an acid-base reaction ($MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O$) from the dissolution of MgO and KH_2PO_4 to the crystallization of hexahydrate, $MgKPO_4 \cdot 6H_2O$ (struvite-K). The MKPC offers excellent performances such as fast-setting, strong bonding, and high early strength (Xu et al., 2015; Wang and Dai, 2017; Wang et al., 2017), which are well suitable for the physical solidification purpose. More importantly, Pb can form highly insoluble pyromorphite ($Pb_5(PO_4)_3X$, $X = Cl^-, OH^-, F^-$) and lead phosphate ($Pb_3(PO_4)_2$) in a phosphate-rich environment. Compared to the $Pb(OH)_2$ that has a relatively high solubility (K_{sp} = ~10^{-4}) produced in high-alkali binders, the pyromorphite and lead phosphate have much lower solubility (K_{sp} = ~10^{-60}-10^{-85} and 10^{-6}, respectively). An excellent resistance of MPC to acid or alkaline attack is also widely recognized (Debela et al., 2013; Mignardi et al., 2012), making it an appealing binder for the S/S treatment of Pb-contaminated soils.

This study aims to elucidate the interactions between the soluble Pb species and the MKPC during the S/S process. Parallel experiments are carried out on the OPC-based S/S process of soluble Pb species, to evaluate how the MKPC interacts with Pb differently from OPC in terms of the environmental acceptability (leachability), strength development, and setting time. The corresponding mechanisms during the hydration of the Pb-containing cement binders are elaborated through thermodynamic and spectroscopic analysis.

2. Materials and methods

2.1. Binders and mix proportions

The OPC (CEM I 52.5N, following the BS EN197–1:2000) was provided by the Green Island Cement (Holdings) Limited (Hong Kong), while the MKPC was prepared using dead-burnt magnesia (DBM) and mono-potassium phosphate (MPP) at an Mg/P molar ratio of 3.0. The powders were mixed for 3 min by a planetary stirrer and water was gradually added at a water-to-cement ratio of 0.3 for producing a homogeneous fresh paste (Table 1). The coal fly ash (CFA) from the Green Island Cement (Holdings) Limited (Hong Kong) was incorporated as a partial replacement of OPC or MKPC to reduce the carbon footprint and increase the S/S efficiency of Pb (Wang et al., 2015a). It should be noted that high-calcium CFA with good crystallinity cannot act as a supplementary cementitious material for secondary hydration, but it can be used for silicate-aluminate-phosphate geopolymerization in MPC (Gardner et al., 2015). As shown in Fig. S1, mullite, quartz, and calcite were detected in the CFA. The chemical compositions of DBM, CFA and OPC were determined by X-ray Fluorescence spectroscopy (AXS GmbH, Bruker), and the results are summarized in Table S1. Because soluble Pb species in Pb-contaminated soils are the major detrimental forms against the S/S process, so the lead nitrate (analytical reagent, Tianjin Damao chemical reagent factory) was used as to investigate the interactions of soluble Pb with the binders in this study.

In order to compare the S/S efficiency of OPC and MKPC, five types of binders were formulated with a Pb-to-cement mass ratio of 0.01 as indicated in Table 1, which represents a high concentration of Pb species (4800 mg kg^{-1}) in contaminated soils based on the guidance manual for use of risk-based remediation goals for contaminated land management in Hong Kong (HK EPD, 2007). Such a high exposure Pb concentration also exists in the actual

Table 1
Mix proportions of binders for Pb immobilization.

	Binders	Ingredients by weight ratio					
		OPC	DBM [a]	MPP [b]	$Pb(NO_3)_2$	CFA	Water [c]
SS1	OPC only	1	–	–	0.01	–	0.3
SS2	OPC + 50% CFA	0.5	–	–	0.01	0.5	0.3
SS3	OPC + 5% MPP	1	–	0.05	0.01	–	0.3
SS4	MKPC only	–	0.493	0.507	0.01	–	0.3
SS5	MKPC + 50% CFA	–	0.247	0.253	0.01	0.5	0.3

[a] As-received magnesia purity = 90.7%.
[b] MgO/MPP molar ratio was set as 3 during the MPC preparation.
[c] Water-to-cement ratio = 0.3.